Supporting Information

Pd-catalyzed CO/vinyl arene copolymerization: when the stereochemistry is controlled by the comonomer

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Experimental

General information. All complex manipulations were performed using standard Schlenk techniques under argon. Deuterated solvents (Cambridge Isotope Laboratories, Inc. (CIL)) were stored as recommended by CIL. Pyridine-2-aldehyde, 2-acetylpyridine, 2-benzoylpyridine, 1- and 2-naphthylamine, 1- and 2-aminoanthracene, TFE and the vinyl arenes were purchased from Sigma-Aldrich and used without further purification for synthetic, spectroscopic and catalytic purposes. Carbon monoxide (purity ≥ 99.9%) was purchased from SIAD and used as it is. Palladium(II) neutral complexes were synthesized using [Pd(cod)(CH_3)Cl], synthesized from [Pd($OCOCH_3$)$_2$] (BASF Italia), benzonitrile (Sigma-Aldrich), HCl 37% (Fluka) and *cis*–*cis*–1,5–cyclooctadiene (Fluka) without further purification. The cationic complexes were synthesized by using $AgPF_6$ and anhydrous acetonitrile (Sigma-Aldrich). Dichloromethane (Sigma-Aldrich) used in the synthesis of Pd complexes was distilled over CaH_2 under argon atmosphere. Mono- and bidimensional NMR spectra were recorded on a Varian 500 spectrometer (500 MHz for ^{1}H, 125.68 MHz for ^{13}C), or on a Varian 400 (400 MHz for ^{1}H, 100.55 MHz for ^{13}C, 376.3 MHz for ^{19}F), using the residual solvent peak as reference (CD_2Cl_2: 5.32 ppm for^{1}H–NMR, 54.00 ppm for ^{13}C–NMR; $CDCl_3$: 7.26 ppm for ^{1}H–NMR, 77.16 ppm for ^{13}C–NMR; CD_3NO_2: 4.33 ppm for ^{1}H-NMR, 62.81 ppm for ^{13}C-NMR).

The average molecular weight (Mw) and polydispersity (Mw/Mn) values of CO/vinyl arene copolymer samples were measured through gel permeation chromatography by using polystyrene standards as the reference. Unless otherwise stated, the mesurements were performed on an Agilent HPLC 1100 (G1310A IsoPump, VWD G1314A detector) with a PLgel 5 μm x 104 Å column, using chloroform as eluent (flow rate 0.6 mL min-1), and for the statistical calculations the Chemstation GPC Data Analysis software was utilized. Samples were prepared by dissolving the copolymer (2 mg) in chloroform (10 mL). The CO/S copolymers obtained with catalysts **6b** and **8b** were dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (120 μL) before adding chloroform.

Caution: HFIP is a very volatile and highly toxic solvent, so proper protection should be used when it is handled.

Synthesis and characterization of ligands and complexes

Synthesis and characterization of ligands 1-9.

Ligands **1** and **2** were synthesized according to the literature procedure.[1, 2]

For ligands **4**, **7**, **9** the following procedure was used:

In a flask equipped with a Dean-Stark apparatus the desired aniline (1 equiv) and pyridine-2-aldehyde (1.5 equiv) are dissolved in toluene, in the presence of an acid catalyst (acetic acid for **4**, **9** and silica-alumina for **7**). The mixture is left under reflux for 6 h, then left to cool and concentrated under reduced pressure until precipitate starts to appear. The precipitation is favoured with the addition of a pentane : diethyl ether mixture (1 : 1). The flask is kept at 248 K overnight, then the obtained solid is filtered off and washed with additional pentane/diethyl ether mixture.

For ligands **3**, **6**, **8** the following procedure was used:

In a flask, 2-acetylpyridine or benzoylpyridine (1 equiv) and 1.1 equiv of $ZnCl_2$ are dissolved in acetic acid. 1 equiv of the desired aniline is then added. The mixture is left under reflux for 3.5 h, then cooled down, and the obtained solid filtered off and washed with petroleum ether. The solid is then dissolved in dichloromethane, to which a 1.00 M solution of sodium (**3**, **6**) or potassium (**8**) oxalate is added. The organic phase is separated and washed with distilled water, then dried over Na_2SO_4. The solution is then separated, and the solvent removed under reduced pressure.

3. (brown oil, 61%) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ = 8.63 (d, 1H, H^6), 8.56 (d, 1H, H^{15}), 8.44 (d, 1H, H^3), 7.91 (t, 1H, H^4), 7.44-7.39 (m, 2H, $H^{5,10}$), 7.19-7.13 (m, 6H, $H^{p,11,14,13,o}$), 7.07 (d, 1H, H^{12}), 6.90 (d, 1H, H^9), 6.48 (t, 2H, H^m); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) δ = 149 (C^{15}), 148 (C^6), 135 (C^{10}), 136 (C^4), 129 (C^{12}), 128 (C^p), 127 (C^o), 125 ($C^{13,14}$), 124 (C^5), 123 ($C^{3,9,11}$), 114 (C^m). Anal. Calcd. for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.08. Found: C, 85.50; H, 5.13; N, 9.00.

4. (yellow solid, 43%) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ = 8.73 (s, 1H, H^i), 8.72 (d, 1H, H^6), 8.27 (d, 1H, H^3), 7.94-7.82 (m, 4H, $H^{4,10}$, $H^{11,14(o12,13)}$), 7.70 (s, 1H, H^{15}), 7.55-7.45 (m, 3H, H^9, $H^{12,13(o11,14)}$), 7.40 (d, 1H, H^5); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) δ = 161.6 (C^i), 150.1 (C^6), 136.9-128.1 ($C^{4,10}$, $C^{11,14(o12,13)}$), 125.6 (C^5), 126.2-121.1 ($C^{12,13(o11,14)}$), 121.8 (C^3), 119.0 (C^{15}). Anal. Calcd. for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.80; H, 5.20; N, 12.00.

6. (brown oil, 65%) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ = 8.61 (m, 2H, $H^{6,14}$), 8.31 (d, 1H, H^3), 7.87 (t, 1H, H^4), 7.76 (d, 1H, H^{11}), 7.66-7.62 (m, 3H, $H^{o,p}$) 7.51-7.36 (m, 3H, $H^{10,12,5}$), 7.18-7.15 (m, 4H, H^{13}), 7.10 (s, 1H, H^{15}), 7.05 (d, 1H, H^9), 6.98-6.95 (m, 2H, H^m); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) δ = 149 ($C^{6,14}$), 137 (C^4), 130 (C^{11}), 129 ($C^{12,o,p}$), 128 (C^{10}), 12 (C^5), 125 (C^9), 124 (C^{13}), 123 (C^3), 122 (C^m) 117 (C^{15}). Anal. Calcd. for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.08. Found: C, 85.60; H, 5.15; N, 9.10.

7. (pale yellow solid, 57%) ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) δ (ppm) = 8.80 (s, 1H, H^i), 8.73 (ddd, 1H, $H^{6'}$), 8.47 (s, 1H, H^{10}), 8.46 (s, 1H, H^9), 8.30 (d, 1H, $H^{3'}$), 8.08 (d, 1H, H^4), 8.05–7.99 (m, 2H, $H^{5,8}$), 7.90–7.82 (m, 2H, $H^{1,4'}$), 7.56 (dd, 1H, H^3), 7.53–7.46 (m, 2H, $H^{6,7}$), 7.41 (ddd, 1H, $H^{5'}$); ^{13}C NMR (75.41 MHz, CD_2Cl_2, 298 K) δ (ppm) = 155.2 (C^i), 150.2 ($C^{6'}$), 137.1 ($C^{4'}$), 129.8 (C^4), 128.6, 128.5 ($C^{5,8}$), 126.9–126.6 ($C^{9,10}$), 126.1, 126.0 ($C^{6,7}$), 125.6 ($C^{5'}$), 122.0 ($C^{3'}$), 121.5 (C^3), 119.0 (C^1). Anal. Calcd. for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.05; H, 5.03; N, 9.90.

8. (ocher solid, 41 %) ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) δ (ppm) = 8.68 (ddd, 1H, $H^{6'}$), 8.44 (s, 1H, H^9), 8.39–8.33 (m, 2H, $H^{10,3'}$), 8.10–7.96 (m, 3H, $H^{8,5,4}$), 7.84 (ddd, 1H, $H^{4'}$), 7.51–7.43 (m, 2H, $H^{6,7}$), 7.40 (ddd, 1H, $H^{5'}$), 7.32 (s, 1H, H^1), 7.12 (dd, 1H, H^3), 2.44 (s, 3H, $CH_3{}^i$); ^{13}C NMR (75.41 MHz, CD_2Cl_2, 298 K) δ (ppm) = 148.9 ($C^{6'}$), 136.7 ($C^{4'}$), 129.9 (C^4), 128.6–128.2 ($C^{5,8}$), 126.4 (C^9), 125.5–125.3 ($C^{6,7,5'}$), 125.4 (C^{10}), 122.1 (C^3), 121.7 ($C^{3'}$), 114.0 (C^1), 16.7 ($CH_3{}^i$). Anal. Calcd. for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45. Found: C, 85.10; H, 5.47; N, 9.40.

9. (brown solid, 58 %) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ (ppm) = 8.92 (s, 1H, H^9), 8.77 (s, 1H, H^i), 8.75 (ddd, 1H, $H^{6'}$), 8.50 (dd, 1H, $H^{3'}$), 8.47 (s, 1H, H^{10}), 8.08–8.03 (m, 2H, $H^{5,8}$), 7.97–7.91 (m, 2H, $H^{4',4}$), 7.53–7.47 (m, 3H, $H^{3,6,7}$), 7.46 (ddd, 1H, $H^{5'}$), 7.13 (d, 1H, H^2); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) δ (ppm) = 161.4 (C^i), 150.0 ($C^{6'}$), 136.8 ($C^{4'}$), 128.8–128.1 ($C^{5,8}$), 126.9 (C^4), 126.4–125.6 ($C^{3,6,7}$), 126.2 (C^{10}), 125.5 ($C^{5'}$), 122.9 (C^9), 122.0 ($C^{3'}$), 111.6 (C^2). Anal. Calcd. for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.10; H, 5.05; N, 9.89.

Synthesis and characterization of the neutral complexes [Pd(N-N')(CH_3)Cl] (N-N'= 1-9), 1a-9a.

General procedure: To 1 equiv. of [Pd(cod)(CH_3)Cl] dissolved in 10 mL of distilled dichloromethane, 1.2 equiv. of ligand were added. The solution was left to stir at room temperature until the appearance of a solid (15 min for **1a**, 30 min for **4a**, **6a**, 45 min for **7a**, **8a**, 1h for **3a**, 1 h 30 min for **2a**, 6h for **9a**). The solution was further concentrated under reduced pressure and diethyl ether was added to favour the complete precipitation of the product. The yellow precipitates were then filtered and washed with additional cold diethyl ether, then dried under vacuum.

Template synthesis for **5a**: 1 equiv of 2-acetylpyridine and 2 drops of formic acid are added to a solution of 1.2 equiv of β-naphthylamine in methanol. The colourless mixture is left to stir at room temperature in the dark, observing the progressive colour change to yellow. After 2.5 h, a suspension of 1 equiv of [Pd(cod)(CH_3)Cl] in methanol is added to the mixture, and the yellow colour intensifies. The mixture is left to stir for an additional 1.5 h, after which the resulting solid is filtered off and washed with cold diethyl ether.

1a. (yellow solid, 92 %) ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) *cis* = 93%, *trans* = 7%. *cis*: δ = 9.14 (d, 1H, H^6), 8.59 (s, 1H, H^i), 8.20 (m, 1H, H^{15}), 8.10 (t, 1H, H^4), 7.98-7.83 (m, 3H, $H^{11,12,3}$), 7.81 (d, 1H, H^5), 7.63-7.51 (m, 3H, $H^{10,13,14}$), 7.23 (d, 1H, H^9), 0.35 (s, 3H, Pd-CH_3). *trans*: δ = 8.75 (d, 1H, H^6), 8.49 (d, 1H, H^i), 8.32-8.30 (m, 1H, H^{15}), 8.16 (m, 1H, H^4), 8.00-7.77 (m, 3H, $H^{11,12,3}$) 7.74 (m, 1H, H^5), 7.63-7.51 (m, 3H, $H^{10,13,14}$), 7.19 (d, 1H, H^9), 1.12 (s, 3H, Pd-CH_3); ^{13}C NMR (100.55 MHz, CD_2Cl_2, 298 K) *cis:* δ = 169.0 (C^i), 150.1 (C^6), 139.4 (C^4), 128.6-127.4 ($C^{11,12,3}$), 127.3-125.5 ($C^{10,13,14}$), 123.4 (C^{15}), 121.4 (C^5), 118.5 (C^9), -1.1 (Pd-CH_3). Anal. Calcd. for $C_{17}H_{15}N_2ClPd$: C, 52.46; H, 3.88; N, 7.20. Found: C, 52.40; H, 3.80; N, 7.00.

2a. (yellow solid, 74 %)^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) *cis* = 96%, *trans* = 4%. *cis*: δ = 9.23 (d, 1H, H^6), 8.12 (t, 1H, H^4), 8.01-7.93 (m, 2H, $H^{12,13}$), 7.90-7.82 (m, 2H, $H^{11,15}$), 7.79 (t, 1H, H^5), 7.62-7.50 (m, 3H, $H^{10,13,14}$), 7.09 (d, 1H, H^9), 2.17 (s, 3H, CH_3^i), 0.11 (s, 3H, Pd-CH_3); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) *cis:* δ = 149.7 (C^6), 139.3 (C^4), 129.2 (C^5), 128.9, 125.6 ($C^{12,13}$), 127.4, 122.7 ($C^{11,15}$), 127.4-125.6 ($C^{10,13,14}$), 118.6 (C^9), 18.9 (CH_3^i), -1.1 (Pd-CH_3). Anal. Calcd. for $C_{18}H_{17}N_2ClPd$: C, 53.62; H, 4.25; N, 6.95. Found: C, 53.70; H, 4.30; N, 7.00.

3a. (orange solid, 57 %) ^{1}H NMR (500 MHz, CD_2Cl_2, 273 K) *cis* = 96% , *trans* = 4%. *cis:* δ = 9.25 (d, 1H, H^6), 8.12 (d, 1H, H^{15}), 7.95 (t, 1H, H^4), 7.81 (t, 1H, H^5), 7.795 (d, 1H, H^{12}), 7.63-7.57 (m, 2H, $H^{11,14}$), 7.53 (t, 1H, H^{13}), 7.36-7.26 (m, 5H, $H^{o',m',3,10,p}$), 7.00 (t, 1H, H^m), 6.94 (d, 1H, H^9), 6.81 (d, 1H, H^o), 0.13 (s, 3H, Pd-CH_3); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 273 K) *cis*: δ = 149 (C^6), 139 (C^4), 130 (C^p), 129 ($C^{12,m,m'}$), 128 ($C^{5,3}$), 127 ($C^{13,14,11}$), 126 ($C^{o,o'}$), 125 (C^{10}), 123 (C^{15}), 119 (C^9), -0.58 (Pd-CH_3). Anal. Calcd. for $C_{23}H_{19}N_2ClPd$: C, 59.37; H, 4.12; N, 6.02. Found: C, 59.33; H, 4.20; N, 6.07.

4a. (yellow solid, 69 %) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) *cis* = 78%, *trans* = 22%. *cis*: δ = 9.11 (d, 1H, H^6), 8.57 (s, 1H, H^i), 8.07 (t, 1H, H^4), 7.98-7.82 (m, 4H, $H^{3,10}$, $H^{11,14(o12,13)}$), 7.76 (t, 1H, H^5), 7.64 (s, 1H, H^{15}), 7.62-7.50 (m, 2H, $H^{12,13(o11,14)}$), 7.37 (d, 1H, H^9), 0.66 (s, 3H, Pd-CH_3). *trans:* δ = 8.68 (d, 1H, H^6), 8.55 (s, 1H, H^i), 8.11 (t, 1H, H^4), 8.00 (s, 1H, H^{15}), 7.98-7.82 (m, 4H, $H^{3,10}$, $H^{11,14(o12,13)}$), 7.70-7.66 (m, 2H, $H^{5,9}$), 7.62-7.50 (m, 2H, $H^{12,13(o11,14)}$), 1.17 (s, 3H, Pd-CH_3); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) *cis:* δ = 167.8 (C^i), 149.9 (C^6), 139.2 (C^4), 129.3-127.3 ($C^{3,10}$, $C^{11,14(o12,13)}$), 129.2 (C^5), 127.4-127.3 ($C^{12,13(o11,14)}$), 122.0 (C^9), 120.2 (C^{15}), -

0.1 (Pd-CH_3). *trans:* δ = 161.5 (C^{i}), 149.1 (C^{6}), 139.2 (C^{4}), 129.3-127.3 ($C^{3,10}$, $C^{11,14(o12,13)}$), 128.6 (C^{5}), 127.4-127.3 ($C^{12,13(o11,14)}$), 122.4 (C^{9}), 121.9 (C^{15}), 0.7 (Pd-CH_3). Anal. Calcd. for $C_{17}H_{15}N_2ClPd$: C, 52.46; H, 3.88; N, 7.20. Found: C, 52.50; H, 3.90; N, 7.25.

5a. (yellow solid, 49 %) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) *cis* = 95%, *trans* = 5%. *cis*: δ = 9.19 (d, 1H, H^{6}), 8.09 (t, 1H, H^{4}), 7.98 (d, 1H, H^{10}) 7.96-7.85 (m, 3H, H^{3}, $H^{11,14(o12,13)}$), 7.76 (t, 1H, H^{5}), 7.61-7.48 (m, 2H, $H^{12,13(o11,14)}$), 7.40 (s, 1H, H^{15}), 7.14 (d, 1H, H^{9}), 2.29 (s, 3H, CH_3^{i}), 0.34 (s, 3H, Pd-CH_3). ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) *cis:* δ = 149.6 (C^{6}), 139.2 (C^{4}), 129.8 (C^{10}), 129.1 (C^{5}), 128.3-125.5 (C^{3}, $C^{11,14(o12,13)}$), 127.5, 126.8 ($C^{12,13(o11,14)}$), 121.5 (C^{9}), 119.5 (C^{15}), 19.1 (CH_3^{i}), -0.1 (Pd-CH_3). Anal. Calcd. for $C_{18}H_{17}N_2ClPd$: C, 53.62; H, 4.25; N, 6.95. Found: C, 53.60; H, 4.28; N, 6.98.

6a. (orange solid, 90 %) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) *cis* = 92% , *trans* = 8%. *cis:* δ = 9.25 (d, 1H, H^{6}), 7.93 (t, 1H, H^{4}), 7.77-7.72 (m, 4H, $H^{5,10,12,15}$), 7.47-7.41 (m, 2H, $H^{13,14}$), 7.35 (d, 1H, H^{3}), 7.30-7.22 (m, 6H, $H^{o,m,p,11}$), 7.08 (d, 1H, H^{9}), 0.43 (s, 3H, Pd-CH_3); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) *cis*: δ = 149 (C^{6}), 139 (C^{4}), 130 (C^{p}), 129 ($C^{12,11,m}$), 128 ($C^{3,5,10,15}$), 127 ($C^{13,14}$), 122 (C^{9}), 121 (C^{o}), 1.4 (Pd-CH_3). Anal. Calcd. for $C_{23}H_{19}N_2ClPd$: C, 59.37; H, 4.12; N, 6.02. Found: C, 59.40; H, 4.18; N, 5.96.

7a. (yellow solid, 94 %)^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) *cis* = 72%, *trans* = 28%. *cis*: δ (ppm) = 9.12 (bd, 1H, $H^{6'}$), 8.63 (s, 1H, H^{i}), 8.51 (s, 2H, $H^{9,10}$), 8.12 (d, 1H, H^{4}), 8.10–8.00 (m, 3H, $H^{4',5,8}$), 7.86 (d, 1H, $H^{3'}$), 7.80 (d, 1H, H^{1}), 7.76 (ddd, 1H, $H^{5'}$), 7.56–7.50 (m, 2H, $H^{6,7}$), 7.38 (dd, 1H, $H^{3'}$), 0.71 (s, 3H, Pd–CH_3). *trans*: δ (ppm) = 8.63 (d, 1H, $H^{6'}$), 8.59 (s, 1H, H^{i}), 8.55 (s, 1H, $H^{10(o9)}$), 8.43 (s,1H, $H^{9(o10)}$), 8.25 (s, 1H, H^{1}), 8.10–8.00 (m, 4H, $H^{4',4,5,8}$), 7.86 (d, 1H, $H^{3'}$), 7.67 (dd, 1H, H^{3}), 7.61 (ddd, 1H, $H^{5'}$), 7.56–7.50 (m, 2H, $H^{6,7}$), 1.18 (s, 3H, Pd–CH_3); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K). *cis*: δ (ppm) = 167.0 (C^{i}), 149.4 ($C^{6'}$), 138.8 ($C^{4'}$), 129.4 (C^{4}), 128.8 ($C^{5'}$), 128.5 ($C^{5,8}$), 126.9 ($C^{3'}$), 126.8 ($C^{9,10}$), 126.1 ($C^{6,7}$), 121.9 (C^{3}), 119.5 (C^{1}), –0.9 (Pd–CH_3). Anal. Calcd. for $C_{21}H_{17}N_2ClPd$: C, 57.42; H, 3.90; N, 6.38. Found: C, 57.38; H, 4.00; N, 6.33.

8a. (yellow solid, 88 %) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) *cis* = 94%, *trans* = 6%. *cis*: δ (ppm) = 9.20 (d, 1H, $H^{6'}$), 8.52 (s, 1H, H^{10}), 8.47 (s, 1H, H^{9}), 8.16 (d, 1H, H^{4}), 8.13–8.00 (m, 3H, $H^{4',5,8}$), 7.95 (d, 1H, $H^{3'}$), 7.79–7.75 (m, 1H, $H^{5'}$), 7.55–7.48 (m, 3H, $H^{1,6,7}$), 7.15 (dd, 1H, H^{3}), 2.34 (s, 3H, CH_3^{K}), 0.40 (s, 3H, Pd–CH_3). *trans*: δ (ppm) = 8.77 (d, 1H, $H^{6'}$), 8.49 (s, 1H, H^{10}), 8.45 (s, 1H, H^{9}), 8.16–8.14 (m, 1H, $H^{4'}$), 8.12–8.01 (m, 3H, $H^{4,5,8}$), 8.00 (d, 1H, $H^{3'}$), 7.71 (dd, 1H, $H^{5'}$), 7.55–7.48 (m, 2H, $H^{6,7}$), 7.22 (dd, 1H, H^{3}), 2.40 (s, 3H, CH_3^{i}), 1.02 (s, 3H, Pd–CH_3); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K). *cis*: δ (ppm) = 149.5 ($C^{6'}$), 139.1 ($C^{4'}$), 130.2 (H^{4}), 128.9 ($C^{5'}$), 128.5–128.2 ($C^{5,8}$), 126.9 (C^{10}), 126.6 (C^{9}), 126.2 ($C^{6,7}$), 125.4 ($C^{3'}$), 121.7 (C^{3}), 118.8 (C^{1}), 19.0 (CH_3^{K}), –0.2 (Pd–CH_3). Anal. Calcd. for $C_{22}H_{19}N_2ClPd$: C, 58.30; H, 4.22; N, 6.18. Found: C, 58.38; H, 4.17; N, 6.23.

9a. (yellow solid, 81 %) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) *cis* = 95%, *trans* = 5%. *cis*: δ (ppm) = 9.18 (d, 1H, $H^{6'}$), 8.72 (s, 1H, H^{9}), 8.67 (s, 1H, H^{i}), 8.55 (s, 1H, H^{10}), 8.12 (dt, 1H, $H^{4'}$), 8.09–8.04 (m, 3H, $H^{4,5,8}$), 7.88 (d, 1H, $H^{3'}$), 7.83 (ddd, 1H, $H^{5'}$), 7.56–7.50 (m, 3H, $H^{3,6,7}$), 7.22 (d, 1H, H^{2}), 0.35 (s, 3H, Pd–CH_3). *trans*: δ (ppm) =8.82 (s, 1H, H^{9}), 8.77 (d, 1H, $H^{6'}$), 8.57 (s, 1H, H^{i}), 8.49 (s, 1H, H^{10}), 8.16 (t, 1H, $H^{4'}$), 8.13–8.04 (m, 2H, $H^{5,8}$), 8.01 (d, 1H, H^{4}), 7.89 (d, 1H, $H^{3'}$), 7.76 (t, 1H, $H^{5'}$), 7.56–7.47 (m, 3H, $H^{3,6,7}$), 7.17 (d, 1H, H^{2}), 1.14 (s, 3H, Pd–CH_3); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K). *cis*: δ (ppm) = 168.8 (C^{i}), 149.7 ($C^{6'}$), 139.1 ($C^{4'}$), 129.3 ($C^{5'}$), 128.7–128.4 ($C^{4,5,8}$), 127.2 ($C^{3'}$), 127.1 (C^{10}), 126.5 ($C^{3(o6,7)}$), 124.3 ($C^{6,7(o3)}$), 122.0 (C^{9}),

117.4 (C^2), –0.9 (Pd–CH_3). Anal. Calcd. for $C_{21}H_{17}N_2ClPd$: C, 57.42; H, 3.90; N, 6.38. Found: C, 57.47; H, 3.88; N, 6.35.

Synthesis and characterization of the cationic complexes [Pd(N-N')(CH_3)($NCCH_3$)][PF_6] (N-N' = 1-9), 1b-9b.

General procedure: To 1 equiv. of the neutral precursor dissolved in 6 mL of distilled dichloromethane, 1.2 equiv. of $AgPF_6$ salt dissolved in 1.5 mL of dry acetonitrile were added. The reaction mixture was left to stir in the dark for 45-90 min (45 min for **1b**-**6b**, 60 min for **7b**, **8b**, 90 min for **9b**). The suspension of AgCl was filtered over Celite® and washed with dichloromethane. The solution was then concentrated under reduced pressure and diethyl ether was added to favour the precipitation of the product. The bright yellow solids were then filtered under reduced pressure, washed with cold diethyl ether and dried under vacuum.

1b. (yellow solid, 70 %) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) *cis* = 31%, *trans* = 69%. *cis:* δ = 8.84 (d, 1H, H^6), 8.58 (s, 1H, H^i), 8.24 (t, 1H, H^4), 8.06 (d, 1H, H^{15}), 8.02-7.91 (m, 4H, $H^{3,5,11,12}$), 7.72-7.55 (m, 3H, $H^{10,13,14}$), 7.25 (d, 1H, H^9), 2.50 (s, 3H, Pd-$NCCH_3$), 0.50 (s, 3H, Pd-CH_3). *trans:* δ = 8.69 (s, 1H, H^i), 8.64 (d, 1H, H^6), 8.38 (d, 1H, H^{15}), 8.31 (t, 1H, H^4), 8.14 (d, 1H, H^3), 8.02-7.91 (m, 2H, $H^{11,12}$), 7.84 (t, 1H, H^5), 7.72-7.55 (m, 3H, $H^{10,13,14}$), 7.31 (d, 1H, H^9), 1.42 (s, 3H, Pd-$NCCH_3$), 1.23 (s, 3H, Pd-CH_3); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) *cis:* δ = 172.7 (C^i), 150.1 (C^6), 140.9 (C^4), 131.3-128.9 ($C^{3,5,11,12}$), 127.9-125.8 ($C^{10,13,14}$), 122.8 (C^{15}), 118.8 (C^9), 3.9 (Pd-CH_3), 3.6 (Pd-$NCCH_3$). *trans*: δ = 164.4 (C^i), 150.1 (C^6), 141.6 (C^4), 131.33-128.9 ($C^{11,12}$), 130.3 (C^3), 129.7 (C^5), 127.9-125.8 ($C^{10,13,14}$), 124.2 (C^{15}), 118.1 (C^9), 3.5 (Pd-CH_3), 2.1 (Pd-$NCCH_3$). Anal. Calcd. for $C_{19}H_{18}N_3F_6PPd$: C, 42.28; H, 3.36; N, 7.79. Found: C, 42.33; H, 3.40; N, 7.83.

2b. (yellow solid, 83 %)^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) *cis* = 65%, *trans* = 35%. *cis:* δ = 8.82 (d, 1H, H^6), 8.26 (t, 1H, H^4), 8.09 (d, 1H, H^3), 8.04-7.87 (m, 3H, $H^{5,11,12}$), 7.76 (d, 1H, H^{15}), 7.69-7.54 (m, 3H, $H^{10,13,14}$), 7.09 (d, 1H, H^9), 2.47 (s, 3H, Pd-$NCCH_3$), 2.28 (s, 3H, $CH_3{}^i$), 0.26 (s, 3H, Pd-CH_3). *trans:* δ = 8.66 (d, 1H, H^6), 8.35 (t, 1H, H^4), 8.17 (d, 1H, H^3), 8.04-7.87 (m, 3H, $H^{11,12,15}$), 7.85 (t, 1H, H^5), 7.69-7.54 (m, 3H, $H^{10,13,14}$), 7.12 (d, 1H, H^9), 2.41 (s, 3H, $CH_3{}^i$), 1.40 (s, 3H, Pd-$NCCH_3$), 1.05 (s, 3H, Pd-CH_3); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) *cis:* δ = 150.3 (C^6), 140.8 (C^4), 131.0-128.1 ($C^{5,11,12}$), 127.7-125.6 ($C^{10,13,14}$), 127.0 (C^3), 122.0 (C^{15}), 118.8 (C^9), 19.3 ($CH_3{}^i$), 3.8 (Pd-CH_3), 3.6 (Pd-$NCCH_3$). *trans:* δ = 150.1 (C^6), 141.6 (C^4), 131.0-128.0 ($C^{11,12}$), 129.6 (C^5), 127.7-125.6 ($C^{10,13,14}$), 123.1 (C^{15}), 117.6 (C^9), 18.2 ($CH_3{}^i$), 3.2 (Pd-CH_3), 1.9 (Pd-$NCCH_3$). Anal. Calcd. for $C_{20}H_{20}N_3F_6PPd$: C, 43.38; H, 3.64; N, 7.59. Found: C, 43.35; H, 3.60; N, 7.55.

3b. (yellow solid, 70 %) ^{1}H NMR (500 MHz, CD_2Cl_2, 253 K) *cis* = 44% , *trans* = 56%. *cis:* δ = 8.87 (d, 1H, H^6), 8.09 (t, 1H, H^4), 8.00-7.97 (m, 2H, $H^{15,5}$), 7.85 (t, 1H, H^{12}), 7.63-7.53 (m, 3H, $H^{11,14,13}$), 7.49 (m, 1H, H^3), 7.36 (d, 1H, $H^{m'}$), 7.35-7.28 (m, 3H, $H^{o',p,10}$), 7.01 (t, 1H, H^m), 6.915 (d, 1H, H^9), 6.79 (d, 1H, H^o), 2.50 (s, 3H, Pd-$NCCH_3$), 0.24 (s, 3H, Pd-CH_3). *trans:* δ = 8.70 (d, 1H, H^6), 8.22 (d, 1H, H^{15}), 8.17 (t, 1H, H^4), 7.90 (d, 1H, H^{12}), 7.85 (t, 1H, H^5), 7.71-7.63 (m, 4H, $H^{3,11,13,14}$), 7.53-7.49 (m, 2H, $H^{o',m'}$), 7.45-7.40 (m, 1H, H^p), 7.35-7.28 (m, 1H, H^{10}), 7.10 (t, 1H, H^m), 6.84 (d, 1H, H^o), 6.76 (d, 1H, H^9), 1.28 (s, 3H, Pd-$NCCH_3$), 1.11 (s, 3H, Pd-CH_3); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 253 K) *cis*: δ = 150 (C^6), 140 (C^4), 131 ($C^{p,5}$), 130.0 (C^3), 129 ($C^{12,m',m}$), 128 (C^{10}), 127 ($C^{11,14,13}$), 126 ($C^{o,o'}$), 120 (C^9), 4.4 (Pd-CH_3), 3.8 (Pd-$NCCH_3$). *trans:* δ

= 150 (C^6), 141 (C^4), 131 ($C^{p,3}$), 130 (C^m), 129 ($C^{m',o'}$), 128 ($C^{5,12}$), 127 ($C^{o,11,14}$), 12 (C^{15}), 118 (C^9), 3.7 (Pd-CH_3), 1.8 (Pd-NCCH_3). Anal. Calcd. for $C_{25}H_{22}N_3F_6PPd$: C, 48.76; H, 3.60; N, 6.82. Found: C, 48.73; H, 3.58; N, 6.78.

4b. (yellow solid, 80%) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) *cis* = 25%, *trans* = 75%. *cis:* δ = 8.77 (d, 1H, H^6), 8.57 (s, 1H, H^i), 8.22 (t, 1H, H^4), 8.07-7.90 (m, 5H, $H^{3,5,10}$, $H^{11,14(o12,13)}$), 7.67-7.57 (m, 3H, $H^{12,13(o11,14)}$, H^{15}), 7.30 (d, 1H, H^9), 2.52 (s, 3H, Pd-NCCH_3), 0.81 (s, 3H, Pd-CH_3). *trans:* δ = 8.68 (s, 1H, H^i), 8.60 (d, 1H, H^6), 8.27 (t, 1H, H^4), 8.12 (d, 1H, H^3), 8.07-7.90 (m, 3H, H^{10}, $H^{11,14(o12,13)}$), 7.86 (s, 1H, H^{15}), 7.80 (t, 1H, H^5), 7.67-7.57 (m, 2H, $H^{12,13(o11,14)}$), 7.52 (d, 1H, H^9), 2.17 (s, 3H, Pd-NCCH_3), 1.27 (s, 3H, Pd-CH_3) ; ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) *trans:* δ = 163.2 (C^i), 149.8 (C^6), 141.6 (C^4), 130.3 (C^3), 130.1 (C^{10}), 129.4 (C^5), 128.8-128.4 ($C^{11,14(o12,13)}$), 128.1 ($C^{12,13(o11,14)}$), 120.8 (C^{15}), 120.7 (C^9), 4.4 (Pd-CH_3), 3.6 (Pd-NCCH_3). Anal. Calcd. for $C_{19}H_{18}N_3F_6PPd$: C, 42.28; H, 3.36; N, 7.79. Found: C, 42.25; H, 3.33; N, 7.74.

5b. (yellow solid, 84 %)^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) *cis* = 50%, *trans* = 50%. *cis:* δ = 8.76 (d, 1H, H^6), 8.24 (t, 1H, H^4), 8.07 (m, 1H, H^3), 8.02 (m, 1H, H^{10}), 7.99-7.85 (m, 3H, $H^{5,11,14}$), 7.65-7.54 (m, 2H, $H^{12,13}$), 7.38 (s, 1H, H^{15}), 7.09 (d, 1H, H^9), 2.49 (s, 3H, Pd-NCCH_3), 2.39 (s, 3H, CH_3^i), 0.49 (s, 3H, Pd-CH_3). *trans*: δ = 8.63 (d, 1H, H^6), 8.30 (t, 1H, H^4), 8.13 (d, 1H, H^3), 8.02 (m, 1H, H^{10}), 7.99-7.85 (m, 2H, $H^{11,14}$), 7.81 (t, 1H, H^5), 7.65-7.54 (m, 2H, $H^{12,13}$), 7.48 (s, 1H, H^{15}), 7.22 (d, 1H, H^9), 2.48 (s, 3H, CH_3^i), 1.70 (s, 3H, Pd-NCCH_3), 1.08 (s, 3H, Pd-CH_3) ; ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) *cis:* δ = 150.2 (C^6), 140.8 (C^4), 130.9 (C^5), 130.2 (C^{10}), 128.4-128.4 ($C^{11,14}$), 128.1-127.7 ($C^{12,13}$), 126.9 (C^3), 120.9 (C^9), 119.8 (C^{16}), 19.6 (CH_3^i), 4.8 (Pd-CH_3), 3.7 (Pd-NCCH_3). *trans:* δ = 150.0 (C^6), 141.6 (C^4), 130.2 (C^{10}), 129.5 (C^5), 128.3 (C^3), 128.4-128.4 ($C^{11,14}$), 128.1-127.7 ($C^{12,13}$), 120.7 (C^9), 119.1 (C^{15}), 18.1 (CH_3^i), 3.3 (Pd-CH_3), 2.8 (Pd-NCCH_3). Anal. Calcd. for $C_{20}H_{20}N_3F_6PPd$: C, 43.38; H, 3.64; N, 7.59. Found: C, 43.40; H, 3.59; N, 7.62.

6b. (yellow solid, 65 %) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) *cis* = 42%, *trans* = 58%. *cis:* δ = 8.87 (d, 1H, H^6), 8.07 (t, 1H, H^4), 7.96 (t, 1H, H^5), 7.80-7.74 (m, 3H, $H^{10,11,14}$), 7.50-7.43 (m, 6H, $H^{3,12,13,m,p}$), 7.47-7.30 (m, 3H, $H^{o,15}$), 7.02 (d, 1H, H^9), 2.53 (s, 3H, Pd-NCCH_3), 0.57 (s, 3H, Pd-CH_3). *trans:* δ = 8.715 (d, 1H, H^6), 8.14 (t, 1H, H^4), 7.80-7.74 (m, 4H, $H^{5,10,11,14}$), 7.61 (d, 1H, H^3), 7.50-7.43 (m, 6H, $H^{12,13,m,p}$), 7.47-7.30 (m, 3H, $H^{o,15}$), 7.07 (d, 1H, H^9), 1.72 (s, 3H, Pd-NCCH_3), 1.21 (s, 3H, Pd-CH_3); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K) *cis*: δ = 15 (C^6), 140 (C^4), 131 (C^3), 130 (C^5), 129 ($C^{m,p,10.o}$) 12 ($C^{11,14}$), 127 ($C^{12,13}$), 122 (C^9), 4.84 (Pd-CH_3), 3.54 (Pd-NCCH_3). *trans:* δ = 150 (C^6), 141 (C^4), 131 (C^3) 130 ($C^{m,p}$) 129 ($C^{5,10,o}$), 128 ($C^{11,14}$), 127 ($C^{12,13}$), 121 (C^9), 3.4 (Pd-CH_3), 2.4 (Pd-NCCH_3). Anal. Calcd. for $C_{25}H_{22}N_3F_6PPd$: C, 48.76; H, 3.60; N, 6.82. Found: C, 48.81; H, 3.63; N, 6.85.

7b. (orange solid, 55 %) ^{1}H NMR (500 MHz, CD_3NO_2, 273 K) *cis* = 17%, *trans* = 83%. *cis*: δ (ppm) = 8.80 (s, 1H, H^i), 8.72 (d, 1H, $H^{6'}$), 8.65–8.57 (m, 2H, $H^{9,10}$), 8.36–8.32 (m, 1H, $H^{4'}$), 8.22–8.10 (m, 4H, $H^{4,3',5,8}$), 7.96–7.92 (m, 2H, $H^{5',1}$), 7.62–7.55 (m, 2H, $H^{6,7}$), 7.42 (dd, 1H, H^3), 2.57 (s, 3H, Pd–NCCH_3), 0.75 (s, 3H, Pd–CH_3). *trans*: δ (ppm) = 8.84 (s, 1H, H^i), 8.68 (d, 1H, H^9), 8.65–8.57 (m, 2H, $H^{6',10}$), 8.36–8.32 (m, 1H, $H^{4'}$), 8.27 (d, 1H, H^4), 8.22–8.10 (m, 4H, $H^{3',1,5,8}$), 7.86 (td, 1H, $H^{5'}$), 7.66 (dd, 1H, H^3), 7.62–7.55 (m, 2H, $H^{6,7}$), 2.31 (s, 3H, Pd–NCCH_3), 1.21 (s, 3H, Pd–CH_3); ^{13}C NMR (125.68 MHz, CD_3NO_2, 273 K). *cis*: δ (ppm) = 173.6 (C^i), 150.5 ($C^{6'}$), 141.6 ($C^{4'}$), 131.1 ($C^{5'}$), 129.8 ($C^{3'}$), 130.4 (C^4), 129.2 ($C^{5,8}$), 128.4–127.4 ($C^{9,10}$), 127.5 ($C^{6,7}$), 122.9 (C^3), 120.9 (C^1), 3.25 (Pd–CH_3), 3.24 (Pd–NCCH_3). *trans*: δ (ppm) = 164.6 (C^i), 150.7 ($C^{6'}$), 142.2 ($C^{4'}$), 131.1 (C^4), 130.7 ($C^{3'}$), 130.0 ($C^{5'}$), 129.2 ($C^{5,8}$), 128.4 (C^9), 127.8

(C^{10}), 127.5 ($C^{6,7}$), 121.8 (C^3), 121.8 (C^1), 3.3 (Pd–CH_3), 3.1 (Pd–$NCCH_3$). Anal. Calcd. for $C_{23}H_{20}N_3F_6PPd$: C, 46.84; H, 3.42; N, 7.12. Found: C, 46.79; H, 3.45; N, 7.08.

8b. (yellow solid, 78 %) ^{1}H NMR (500 MHz, CD_3NO_2, 273 K) *cis* = 48%, *trans* = 52%. *cis*: δ (ppm) = 8.75 (dd, 1H, $H^{6'}$), 8.63 (s, 1H, H^{10}), 8.58 (s, 1H, H^9), 8.35 (dt, 1H, $H^{4'}$), 8.32–8.24 (m, 2H, $H^{4,3'}$), 8.14–8.08 (m, 2H, $H^{5,8}$), 7.94 (ddd, 1H, $H^{5'}$), 7.68 (s, 1H, H^1), 7.59–7.55 (m, 2H, $H^{6,7}$), 7.24 (dd, 1H, H^3), 2.54 (s, 3H, Pd–$NCCH_3$), 2.53 (s, 3H, CH_3^K), 0.43 (s, 3H, Pd–CH_3). *trans*: δ (ppm) = 8.68 (dd, 1H, $H^{6'}$), 8.63 (s, 1H, H^{10}), 8.60 (s, 1H, H^9), 8.38 (dt, 1H, $H^{4'}$), 8.32–8.24 (m, 2H, $H^{4,3'}$), 8.14–8.08 (m, 2H, $H^{5,8}$), 7.88 (ddd, 1H, $H^{5'}$), 7.77 (s, 1H, H^1), 7.59–7.55 (m, 2H, $H^{6,7}$), 7.38 (dd, 1H, H^3), 2.60 (s, 3H, CH_3^K), 1.83 (s, 3H, Pd–$NCCH_3$), 1.02 (s, 3H, Pd–CH_3); ^{13}C NMR (125.68 MHz, CD_3NO_2, 273 K). *cis*: δ (ppm) = 149.9 ($C^{6'}$), 141.8 ($C^{4'}$), 131.0 (C^4), 130.7 ($C^{5'}$), 129.8–128.3 ($C^{5,8}$), 128.1 (C^4), 127.7 (C^{10}), 127.5 (C^9), 127.2–126.2 ($C^{6,7}$), 122.4 (C^3), 120.3 (C^1), 19.7 (CH_3^K), 3.5 (Pd–CH_3), 3.4 (Pd–$NCCH_3$). *trans*: δ (ppm) = 150.6 ($C^{6'}$), 142.0 ($C^{4'}$), 130.8 (C^4), 129.8 ($C^{5'}$), 129.8–128.3 ($C^{5,8}$), 129.0 (C^4), 127.6 (C^{10}), 127.4 (C^9), 127.2–126.2 ($C^{6,7}$), 122.5 (C^3), 119.6 (C^1), 18.2 (CH_3^K), 2.5 (Pd–$NCCH_3$), 2.1 (Pd–CH_3). Anal. Calcd. for $C_{24}H_{22}N_3F_6PPd$: C, 47.74; H, 3.67; N, 6.96. Found: C, 47.79; H, 3.65; N, 6.98.

9b. (orange/red brick solid, 95 %) ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) *cis* = 35%, *trans* = 65%. *cis*: δ (ppm) = 8.88 (d, 1H, $H^{6'}$), 8.66 (s, 1H, H^i), 8.60 (s, 1H, H^9), 8.59 (s, 1H, H^{10}), 8.31 (dt, 1H, $H^{4'}$), 8.21–8.17 (m, 2H, $H^{5,8}$), 8.14–8.07 (m, 1H, H^4), 8.04 (d, 1H, $H^{3'}$), 8.01 (dd, 1H, $H^{5'}$), 7.63–7.56 (m, 2H, $H^{6,7}$), 7.55 (t, 1H, H^3), 7.25 (d, 1H, H^2), 2.49 (s, 3H, Pd–$NCCH_3$), 0.48 (s, 3H, Pd–CH_3). *trans*: δ (ppm) = 8.91 (s, 1H, H^9), 8.78 (s, 1H, H^i), 8.67 (d, 1H, $H^{6'}$), 8.58 (s, 1H, H^{10}), 8.33 (dt, 1H, $H^{4'}$), 8.17 (d, 1H, $H^{3'}$), 8.14–8.07 (m, 3H, $H^{4,5,8}$), 7.86 (dt, 1H, $H^{5'}$), 7.63–7.56 (m, 3H, $H^{6,7,3}$), 7.31 (d, 1H, H^2), 1.25 (s, 3H, Pd–CH_3), 1.05 (s, 3H, Pd–$NCCH_3$); ^{13}C NMR (125.68 MHz, CD_2Cl_2, 298 K). *cis*: δ (ppm) = 172.4 (C^i), 150.7 ($C^{6'}$), 140.7 ($C^{4'}$), 131.0 ($C^{5'}$), 130.0 (C^4), 128.7 ($C^{3'}$), 128.5 ($C^{5,8}$), 127.6 (C^{10}), 127.0–126.8 ($C^{6,7}$), 124.3 (C^3), 121.2 (C^9), 118.0 (C^2), 4.0 (Pd–CH_3). *trans*: 163.9 (C^i), 149.8 ($C^{6'}$), 141.4 ($C^{4'}$), 130.2 ($C^{3'}$), 130.0 (C^4),129.5 ($C^{5'}$), 128.4 ($C^{5,8}$), 127.2 (C^{10}), 127.0–126.8 ($C^{6,7}$), 125.0 (C^3), 123.2 (C^9), 117.2 (C^2), 4.3 (Pd–CH_3), 1.7 (Pd–$NCCH_3$). Anal. Calcd. for $C_{23}H_{20}N_3F_6PPd$: C, 46.84; H, 3.42; N, 7.12. Found: C, 46.88; H, 3.47; N, 7.16.

CO/vinyl arene copolymerization reactions.

All the catalytic experiments were carried out at atmospheric carbon monoxide pressure in a three-necked, thermostated 75 mL glass reactor equipped with a magnetic stirrer. After establishment of the reaction temperature (303 K), the precatalyst (n_{Pd} = 12.7 x 10^{-6} mol), 1,4-benzoquinone ([BQ]/[Pd] = 5), vinyl arene (10 mL, [S]/[Pd] = 6800; [MS]/[Pd] = 6000; [TBS]/[Pd] = 4300) and TFE (20 mL) were added. CO was bubbled through the solution for 10 min; afterwards two 4 L balloons previously filled with CO were connected to the reactor. After the desired time (24 h), the reaction mixture was poured into 100 mL of methanol and stirred for 1.5 h at room temperature. The solid was filtered off and washed thoroughly with methanol, then dried under vacuum to constant weight. In the case of the copolymerization of CO/TBS with complexes **1b**, **7b** and **9b**, since the product could not be recovered directly from the filter, it was dissolved in chloroform, and upon removal of the solvent a green glass-like solid was obtained.

For the CO/FS copolymerization an analogous procedure is followed but using a 50 mL reactor and with quantities of reagents and reaction conditions reported in Table 6.

Preparation of copolymer samples for NMR characterization.

70 mg of copolymer are weighted and dissolved in 0.70 mL of HFIP, to which 1.40 mL of $CDCl_3$ are then added. 0.70 mL of the resulting solution are taken and used for the NMR analysis.

Recrystallization of CO/vinyl arene polyketones.

The polyketones were recrystallized to eliminate any possible trace of palladium metal due to decomposition of the catalyst. 250 mg of copolymer are dissolved in 20 mL of chloroform (or more, depending on the copolymer solubility). The solution is left to stir until complete dissolution of the copolymer, then filtered over Celite® and washed with additional chloroform. The solvent is partially removed until few milliliters of solution are obtained. The solution is slowly dropped into 40 mL of ethanol, observing precipitation of a white solid that is then filtered off, washed with additional ethanol and left to dry under reduced pressure.

For the polyketones unsoluble in chloroform another procedure is applied: 200 mg of copolymer are suspended in 20 mL of ethyl acetate and left under stirring at room temperature for 4 h. The polymer is then filtered off, washed with the same solvent and dried, and then re-suspended in diethyl ether and left to stir at room temperature for an additional 2 h. The solid is then filtered off, washed with diethyl ether and dried under vacuum.

NMR characterization of ligands and complexes.

NMR characterization of ligand 1 (CD_2Cl_2, T = 298 K)

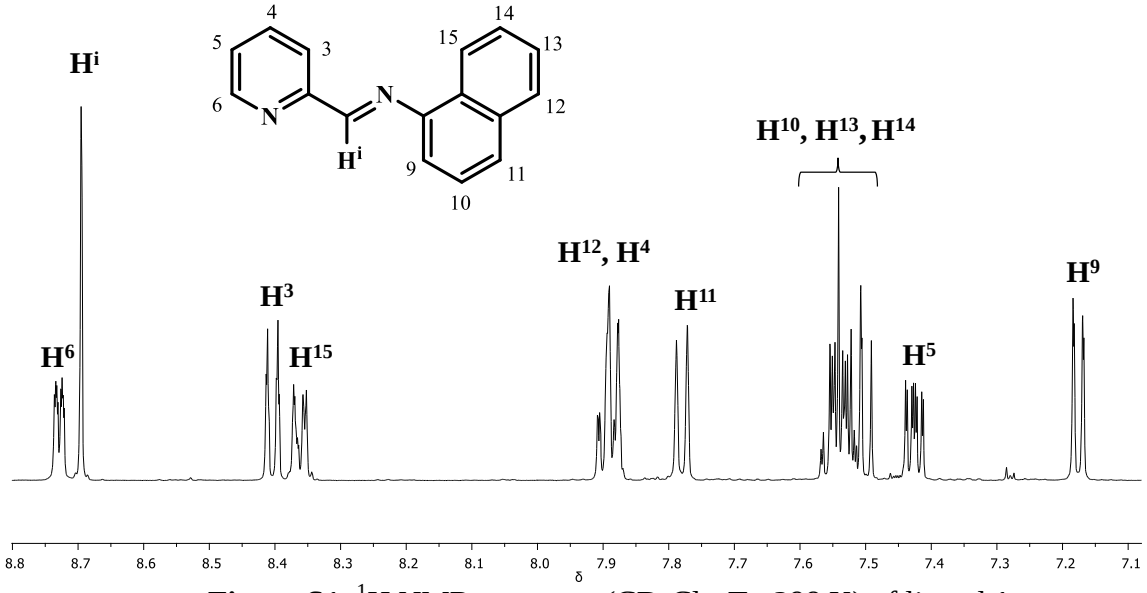

Figure S1. ^{1}H NMR spectrum (CD_2Cl_2, T= 298 K) of ligand **1**.

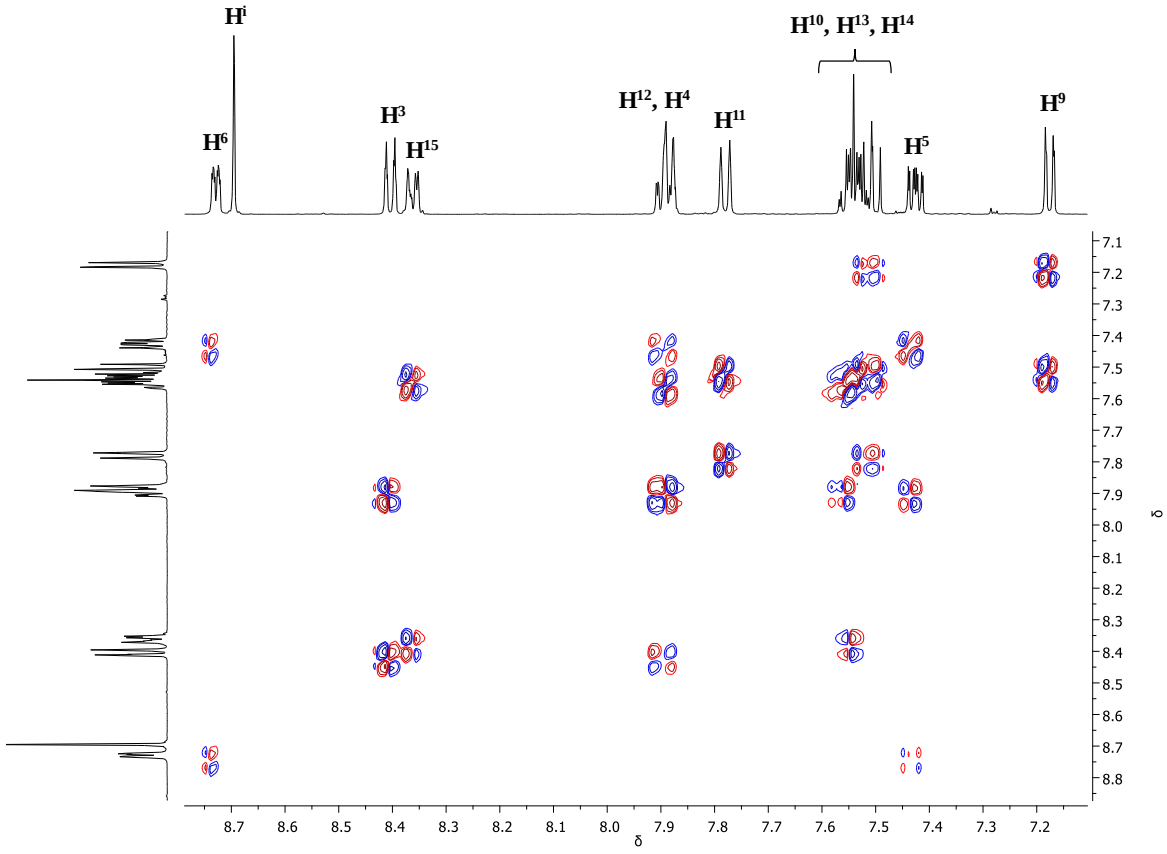

Figure S2. $^{1}H,^{1}H$-DQCOSY spectrum (CD_2Cl_2, T= 298 K) of ligand **1**.

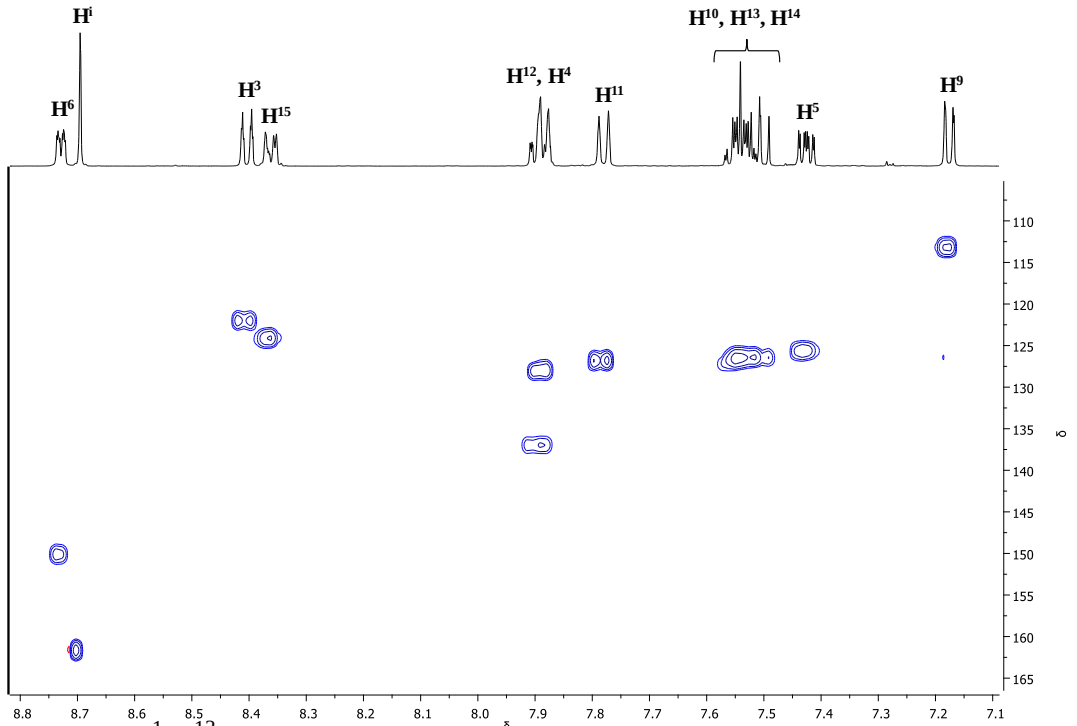

Figure S3. $^{1}H,^{13}C$-HSQC spectrum (CD_2Cl_2, T= 298 K) of ligand **1** (Blue = CH/CH_3).

NMR characterization of ligand 2 (CD_2Cl_2, T = 298 K)

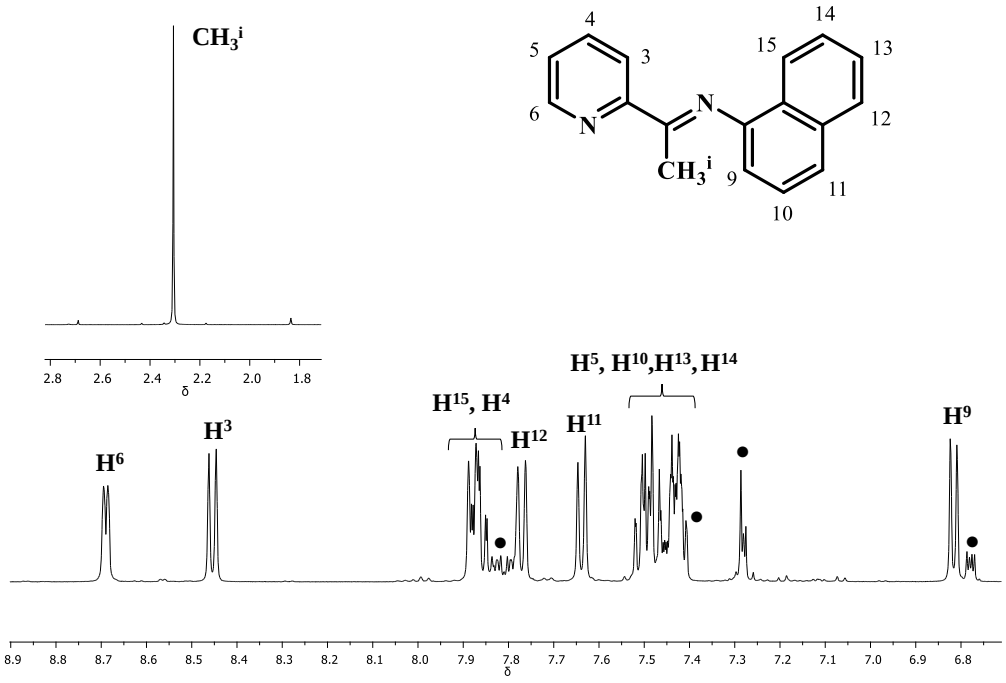

Figure S4. ^{1}H NMR spectrum (CD_2Cl_2, T= 298 K) of ligand **2** with traces of α-naphthylamine (●).

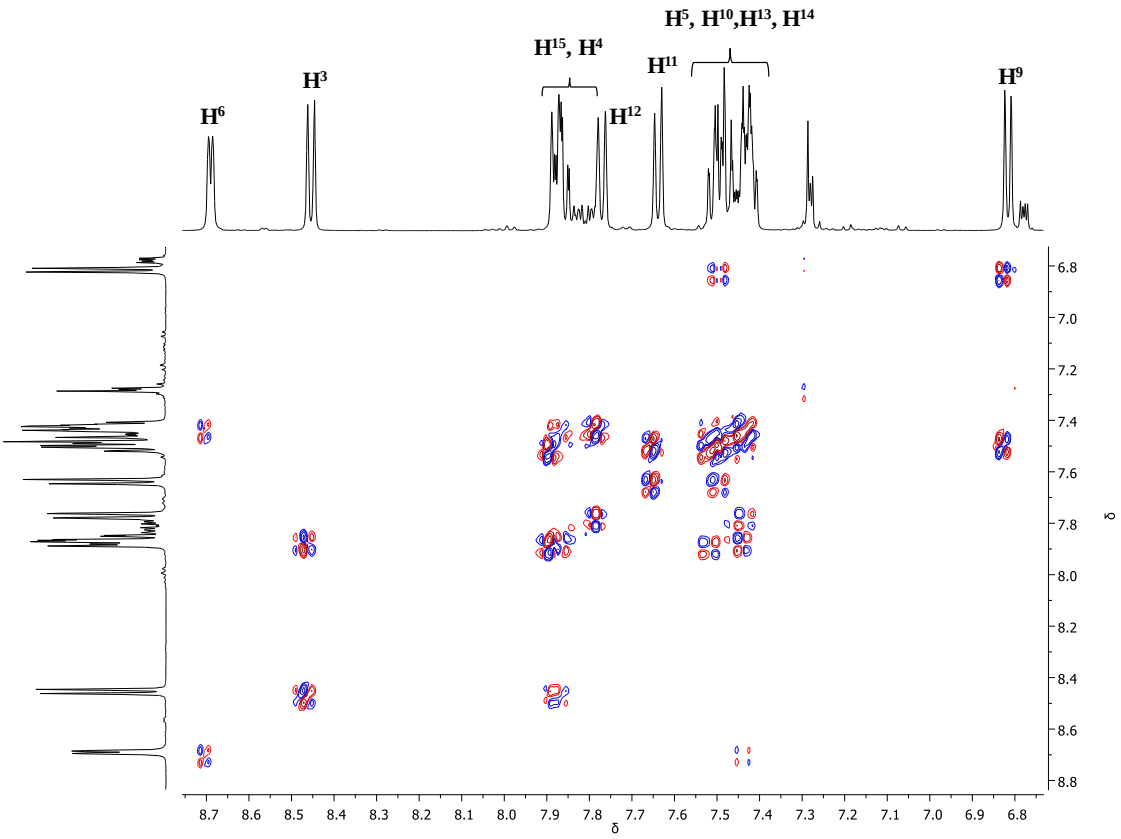

Figure S5. ^{1}H,^{1}H-DQCOSY spectrum (CD_2Cl_2, T= 298 K) of ligand **2**.

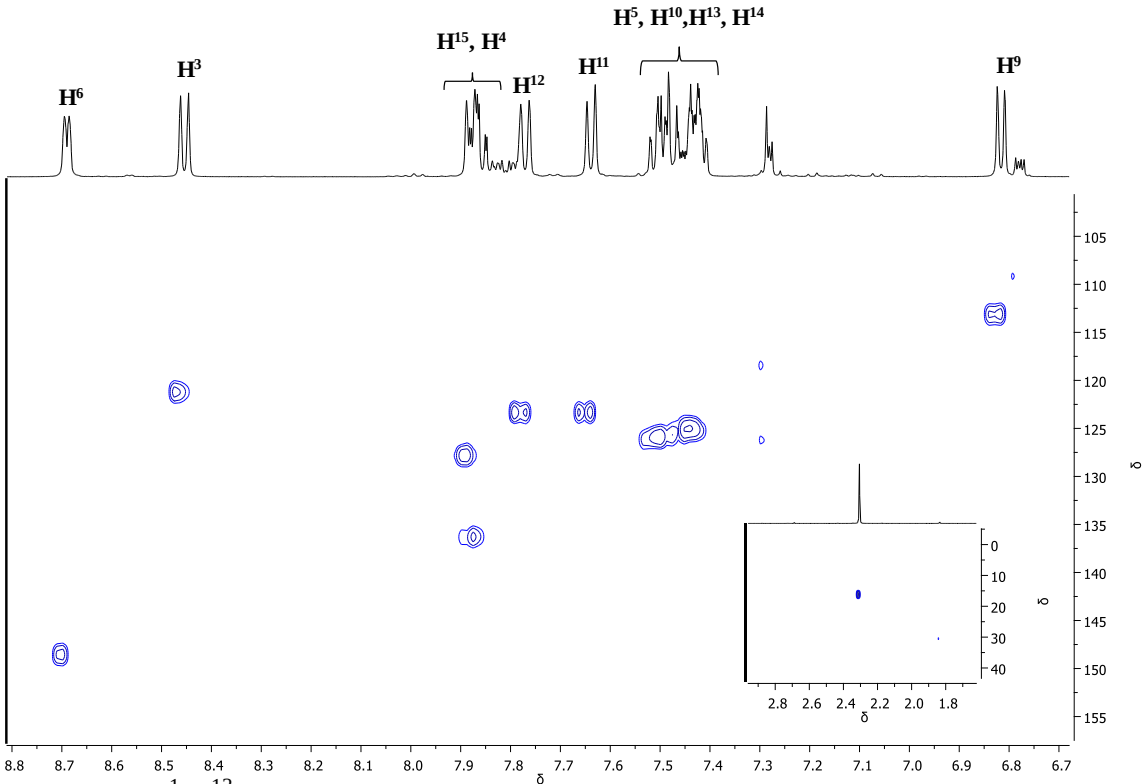

Figure S6. $^{1}H,^{13}C$-HSQC spectrum (CD_2Cl_2, T= 298 K) of ligand **2 (**Blue = CH/CH_3).

NMR characterization of ligand 3 (CD_2Cl_2, T = 298 K)

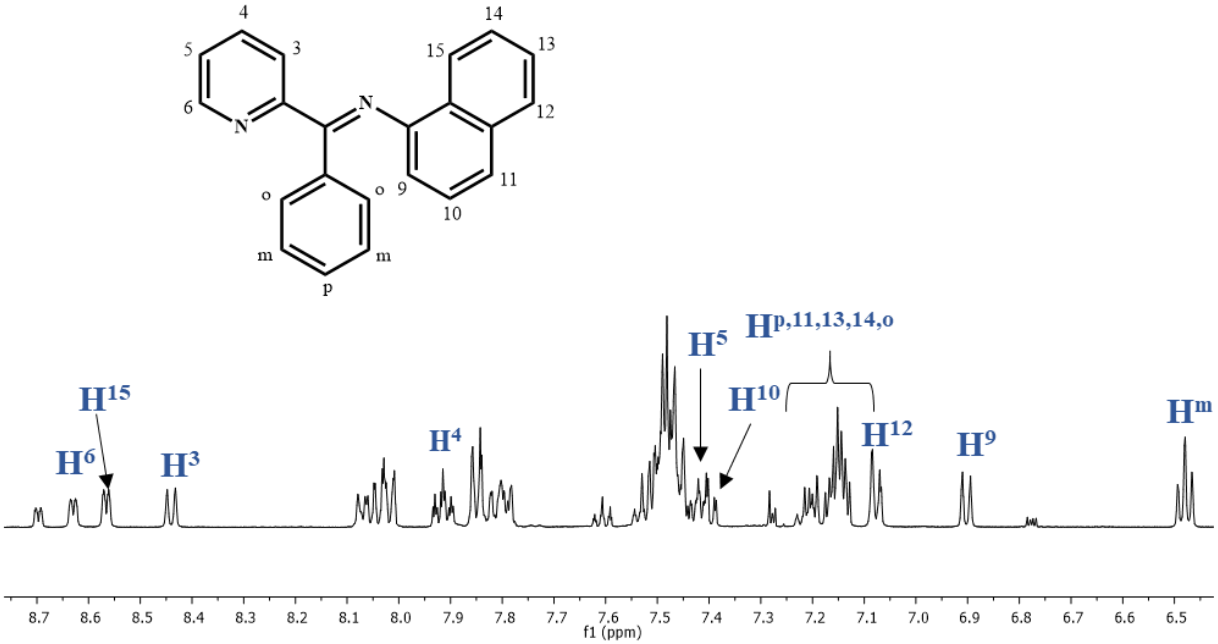

Figure S7. ^{1}H NMR spectrum (CD_2Cl_2, T = 298 K) of **3** (residual peaks of benzoylpyridine and α-naphthylamine).

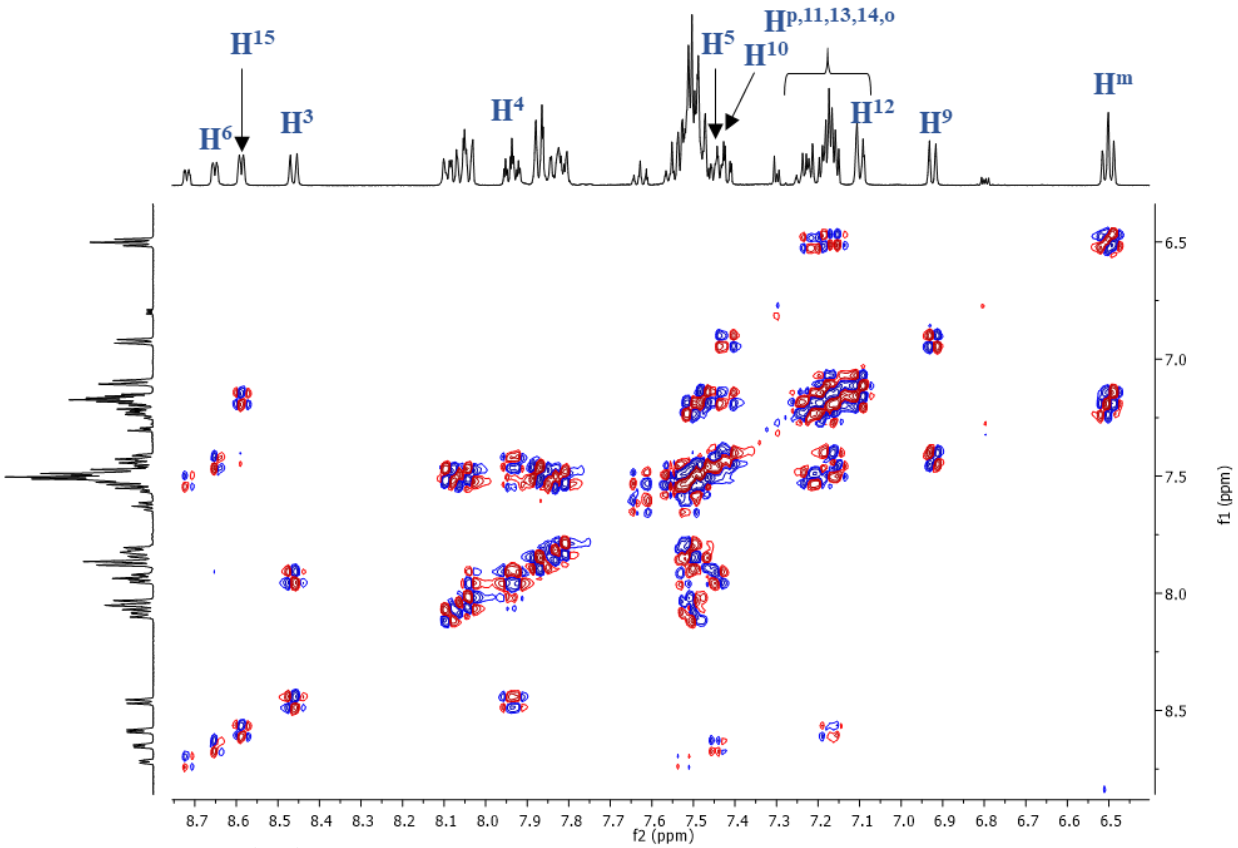

Figure S8. ^{1}H,^{1}H-DQCOSY spectrum (CD_2Cl_2, T = 298 K) of **3** (residual peaks of benzoylpyridine and α-naphthylamine).

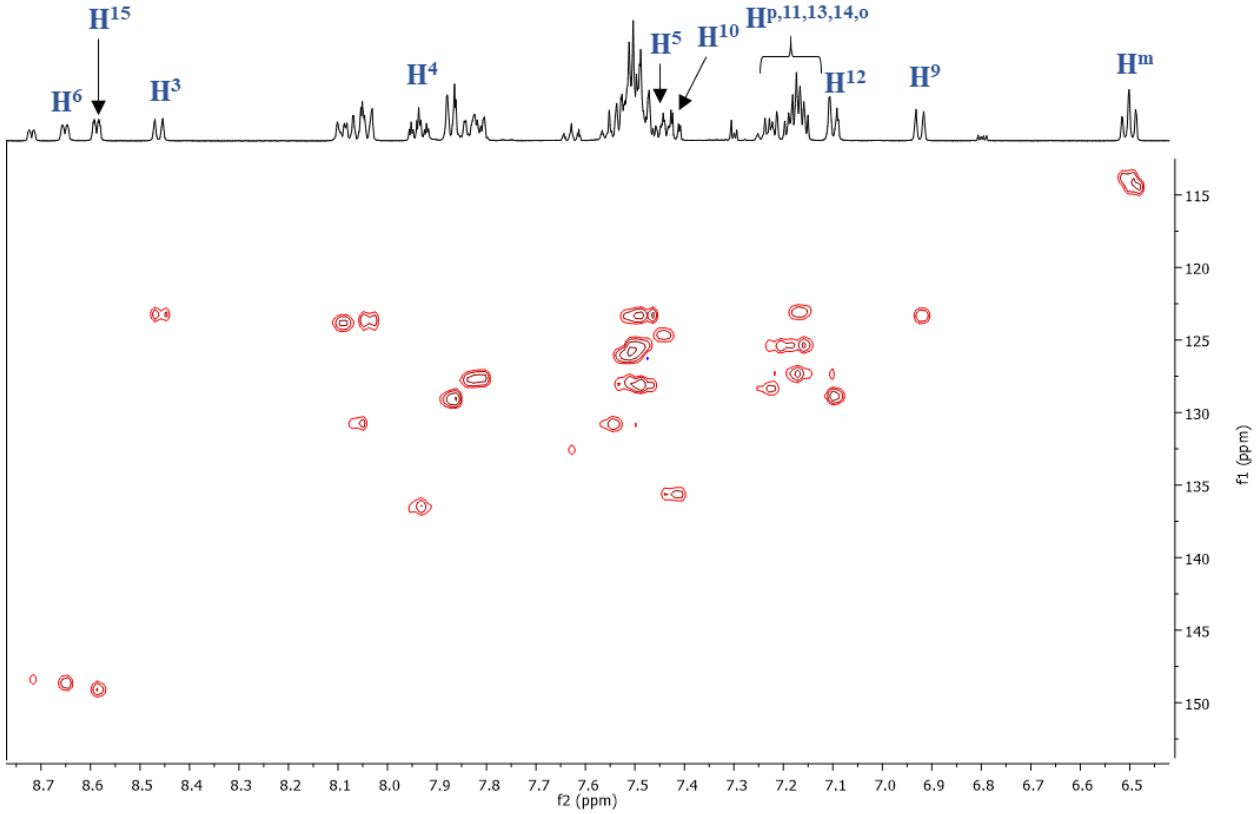

Figure S9. ^{1}H,^{13}C-HSQC spectruum (CD_2Cl_2, T = 298 K) of **3** (residual peaks of benzoylpyridine and α-naphthylamine; red = CH/CH_3).

NMR characterization of ligand 4 (CD_2Cl_2, T = 298 K)

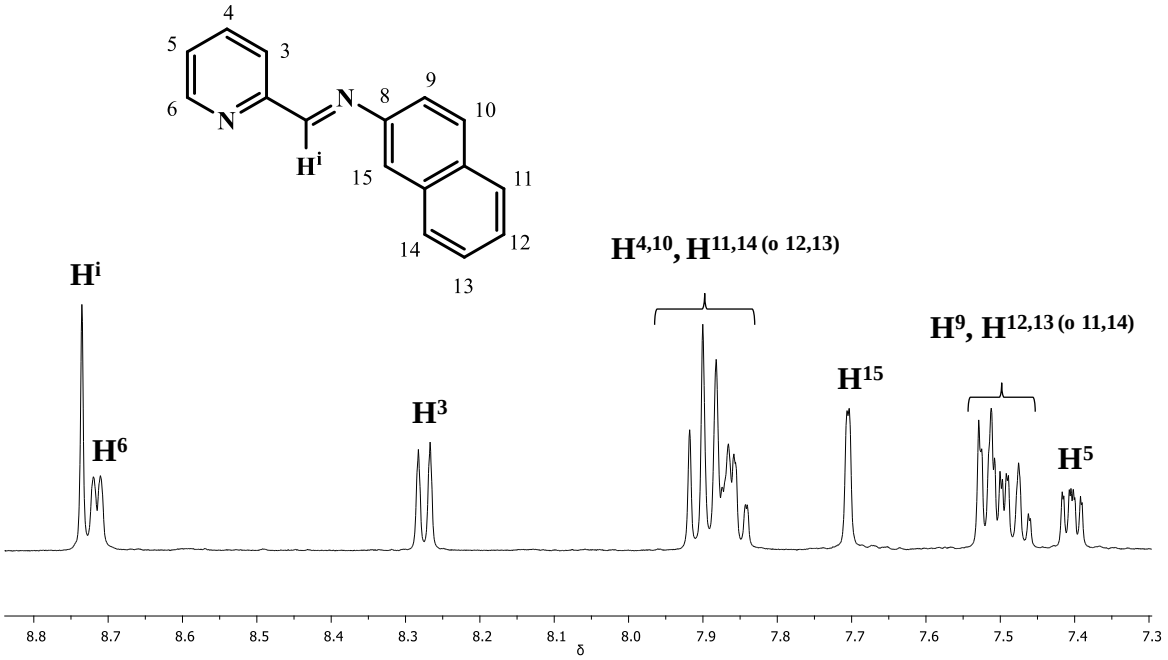

Figure S10. ^{1}H NMR spectrum (CD_2Cl_2, T= 298 K) of ligand **4**.

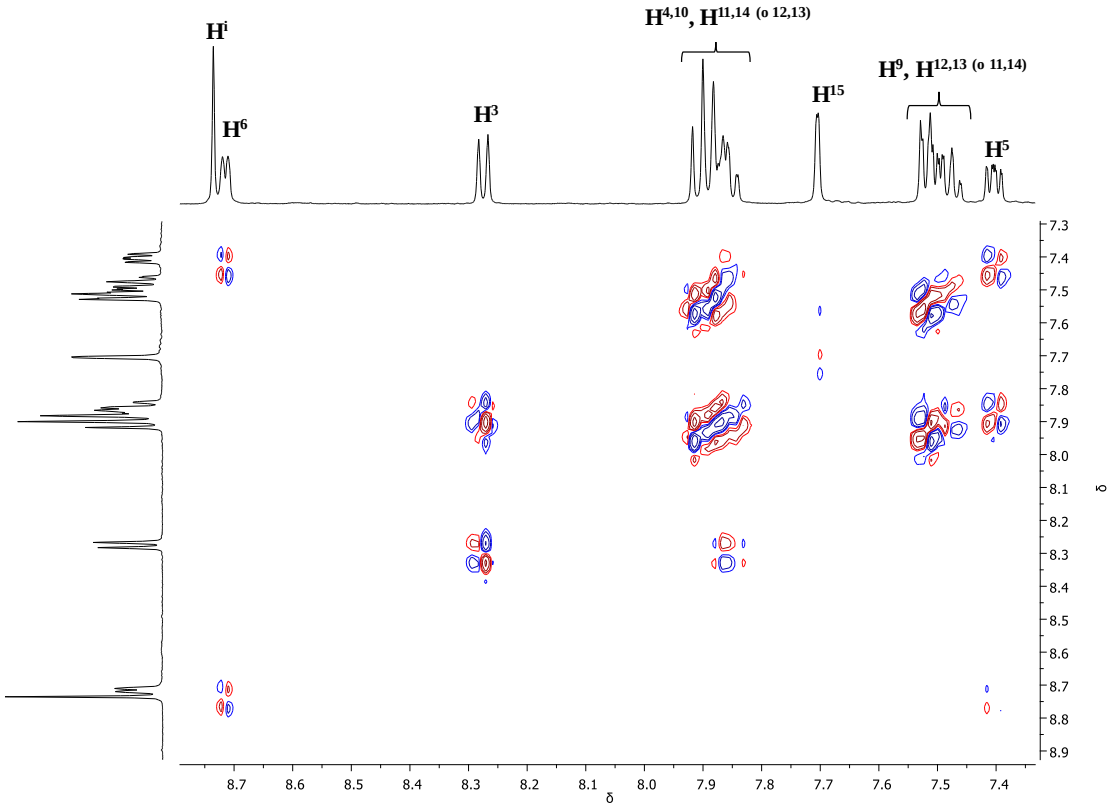

Figure S11. ^{1}H,^{1}H-DQCOSY spectrum (CD_2Cl_2, T= 298 K) of ligand **4**.

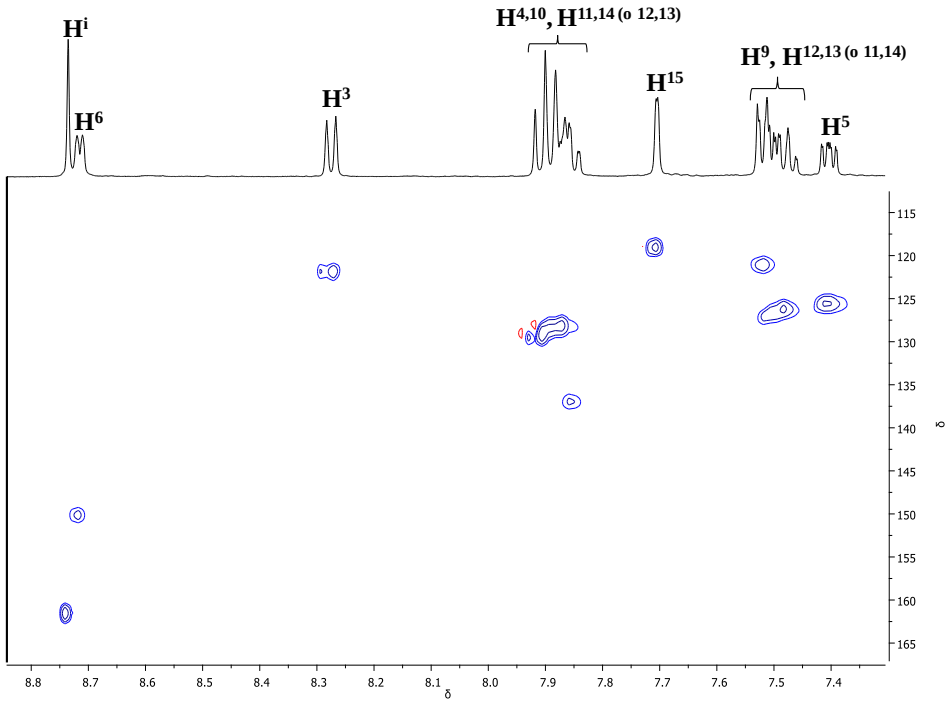

Figure S12. $^{1}H,^{13}C$-HSQC spectrum (CD_2Cl_2, T=298 K) of ligand **4**.

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NMR characterization of ligand 6 (CD_2Cl_2, T = 298 K)

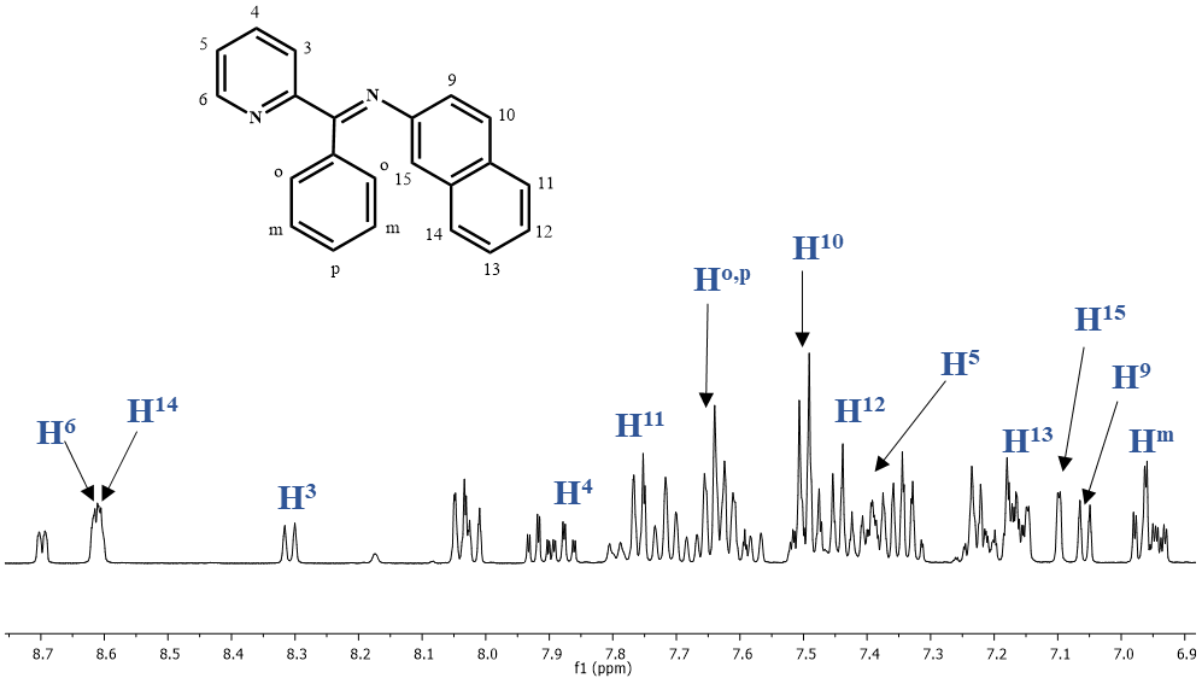

Figure S13. ^{1}H NMR spectrum (CD_2Cl_2, T = 298 K) of **6** (residual peaks of benzoylpyridine and β-naphthylamine).

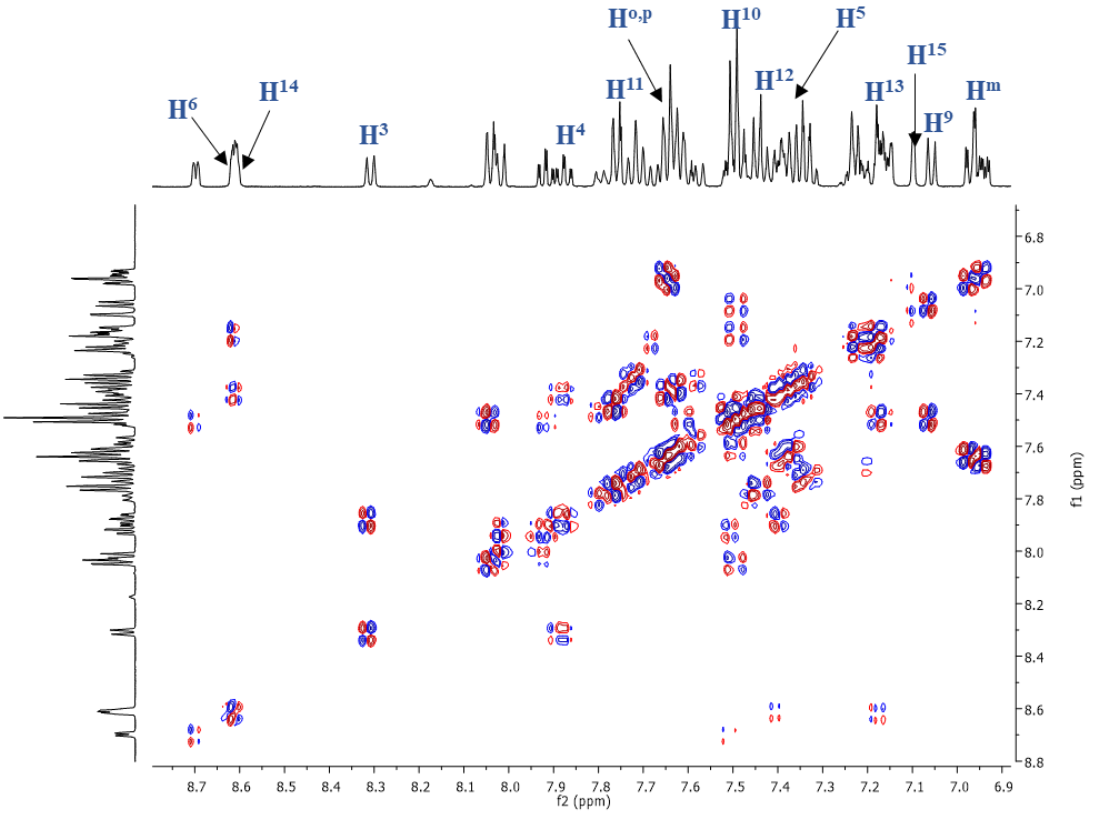

Figure S14. ^{1}H,^{1}H-DQCOSY spectrum (CD_2Cl_2, T = 298K) of **6** (residual peaks of benzoylpyridine and β-naphthylamine).

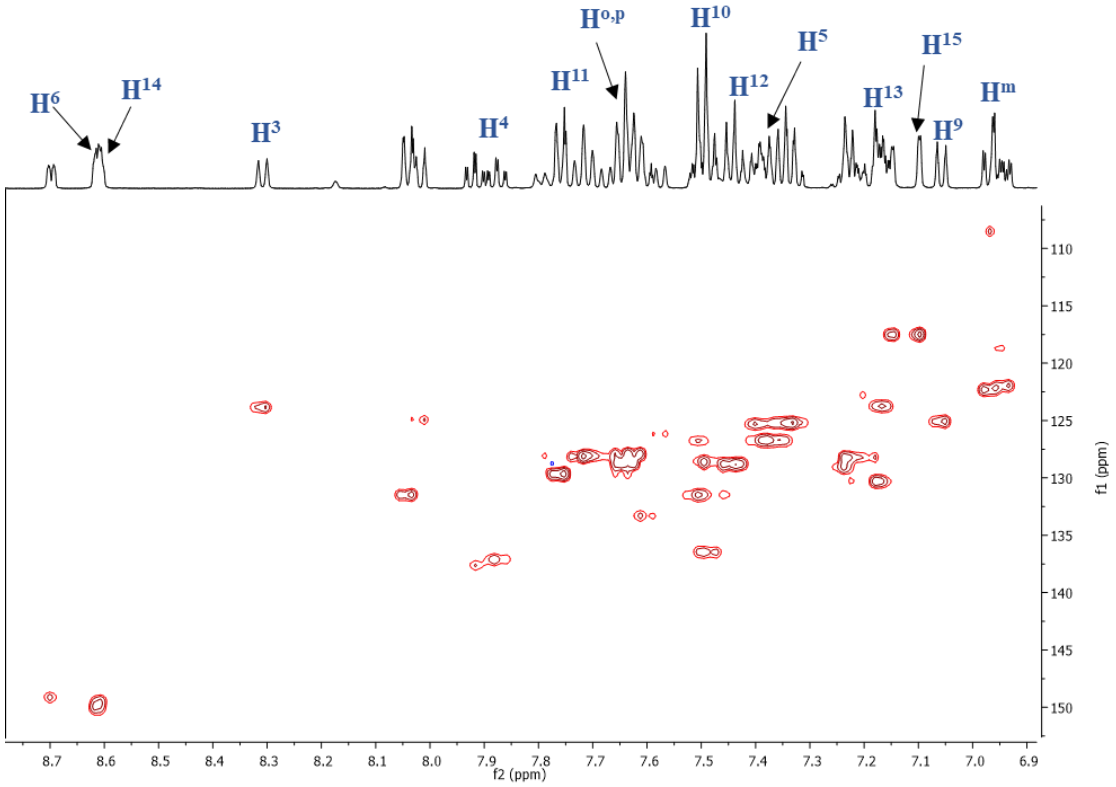

Figure S15. ^{1}H,^{13}C-HSQC spectrum (CD_2Cl_2, T = 298 K) of **6** (residual peaks of benzoylpyridine and β-naphthylamine; red = CH/CH_3).

NMR characterization of ligand 7 (CD_2Cl_2, T = 298 K)

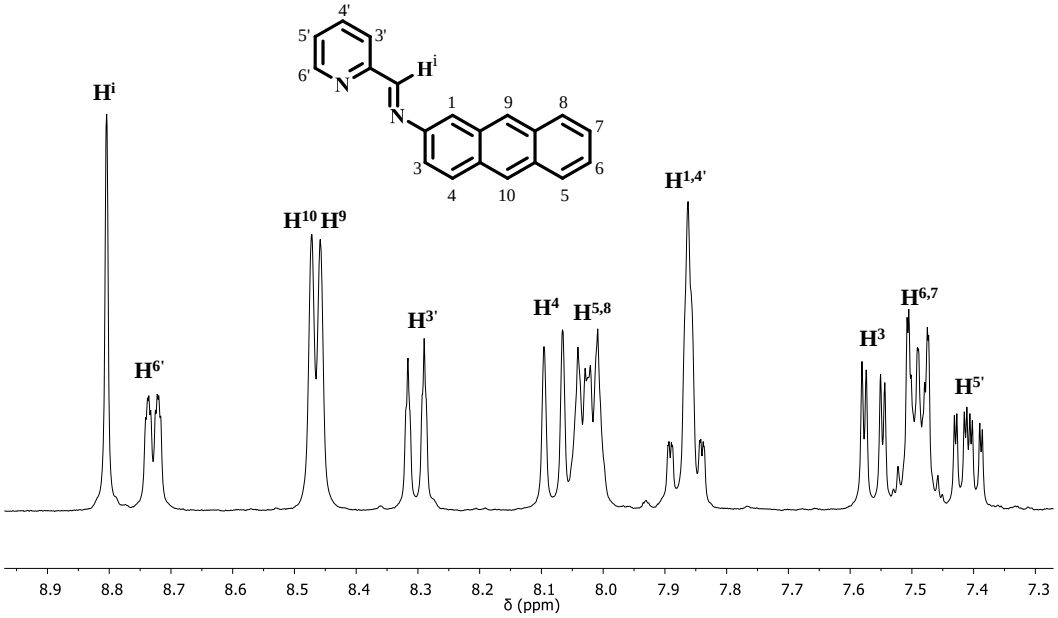

Figure S16. ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of ligand **7**.

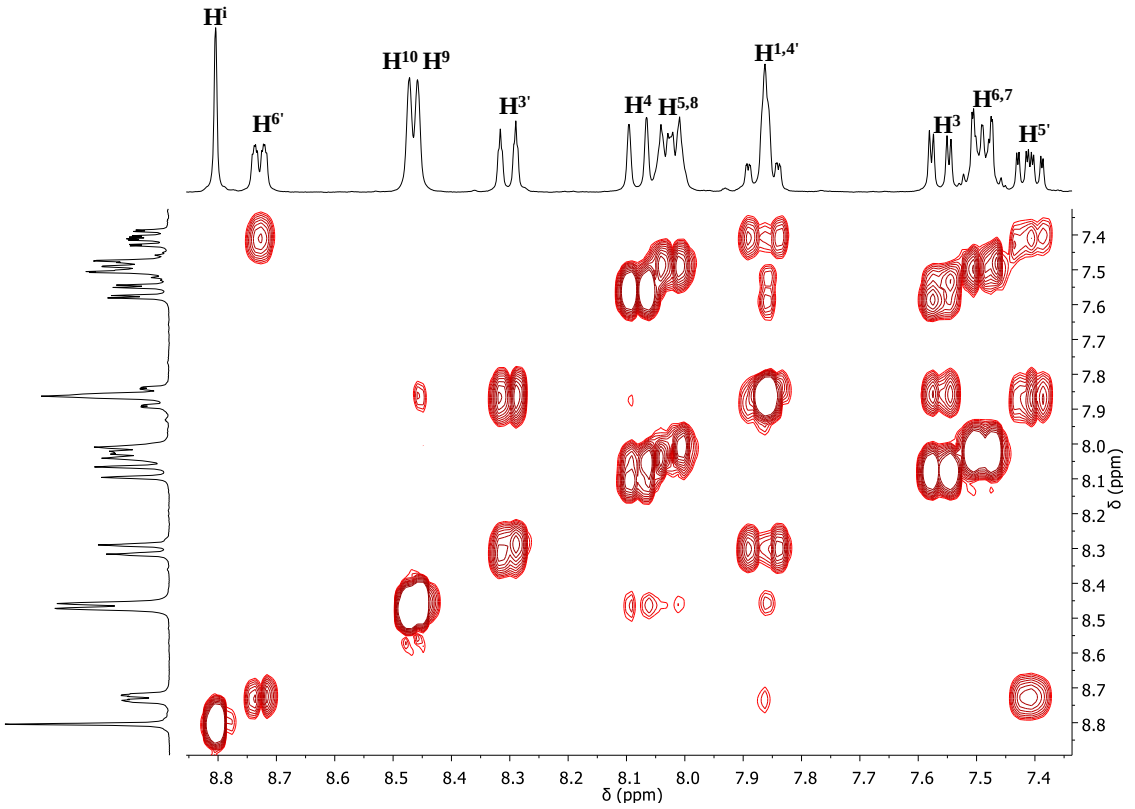

Figure S17. ^{1}H,^{1}H-COSY spectrum (CD_2Cl_2, 298 K) of ligand **7**.

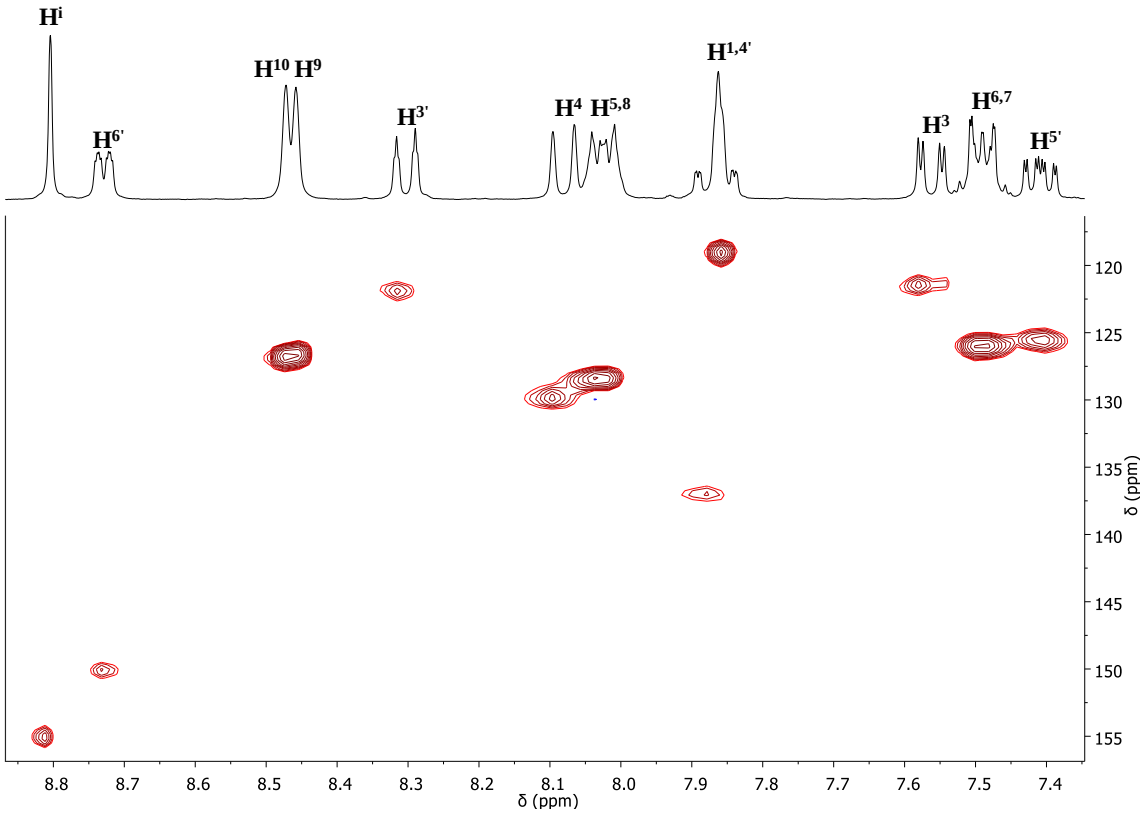

Figure S18. $^{1}H,^{13}C$-HSQC spectrum (CD_2Cl_2, 298 K) of ligand **7** (red = CH/CH_3).

NMR characterization of ligand 8 (CD_2Cl_2, T = 298 K)

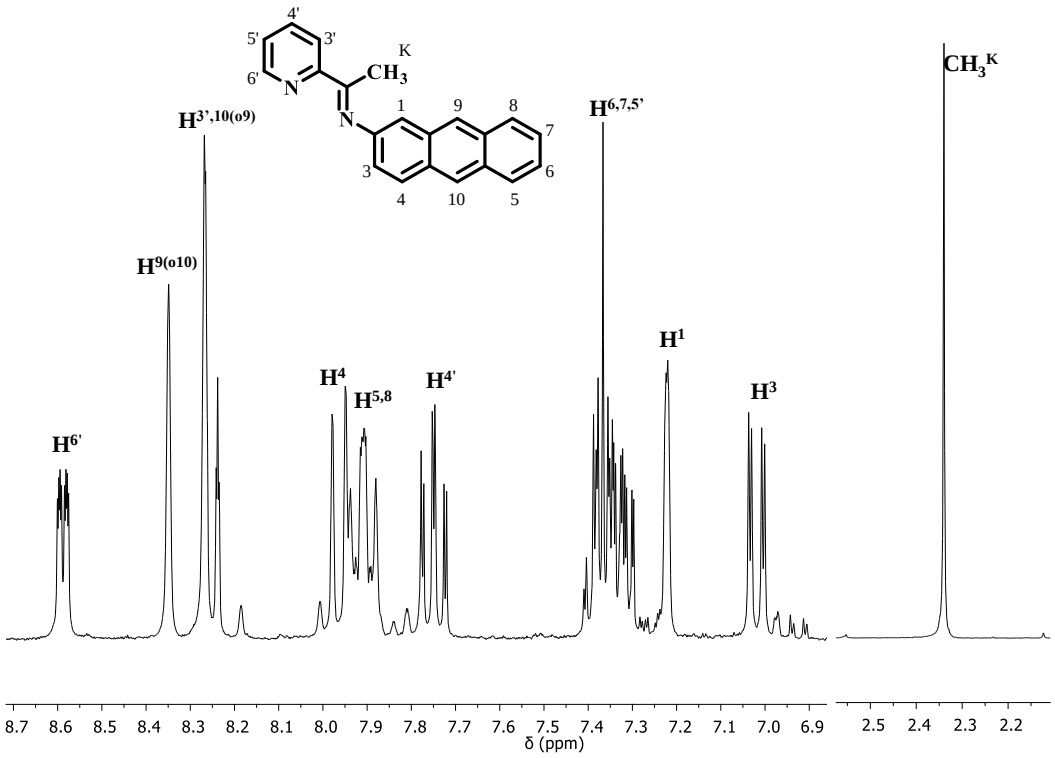

Figure S19. ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of ligand **8**. Aromatic and aliphatic region not on scale.

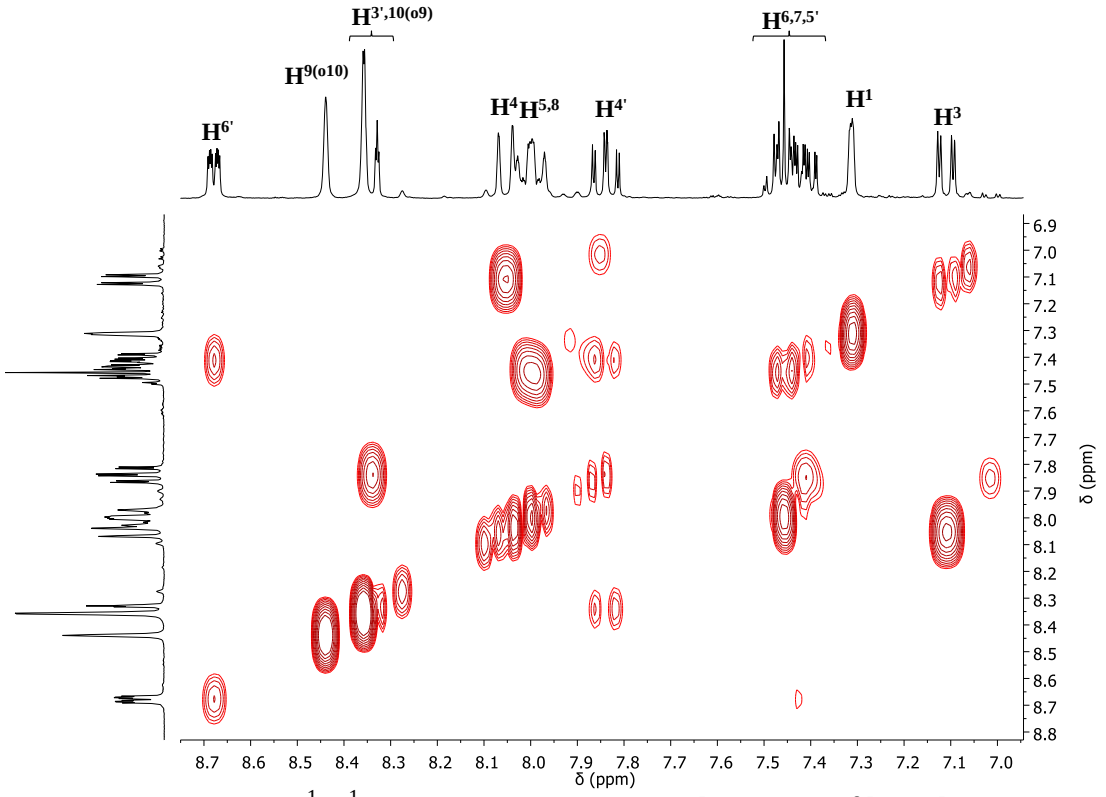

Figure S20. $^{1}H,^{1}H$-COSY spectrum (CD_2Cl_2, 298 K) of ligand **8**.

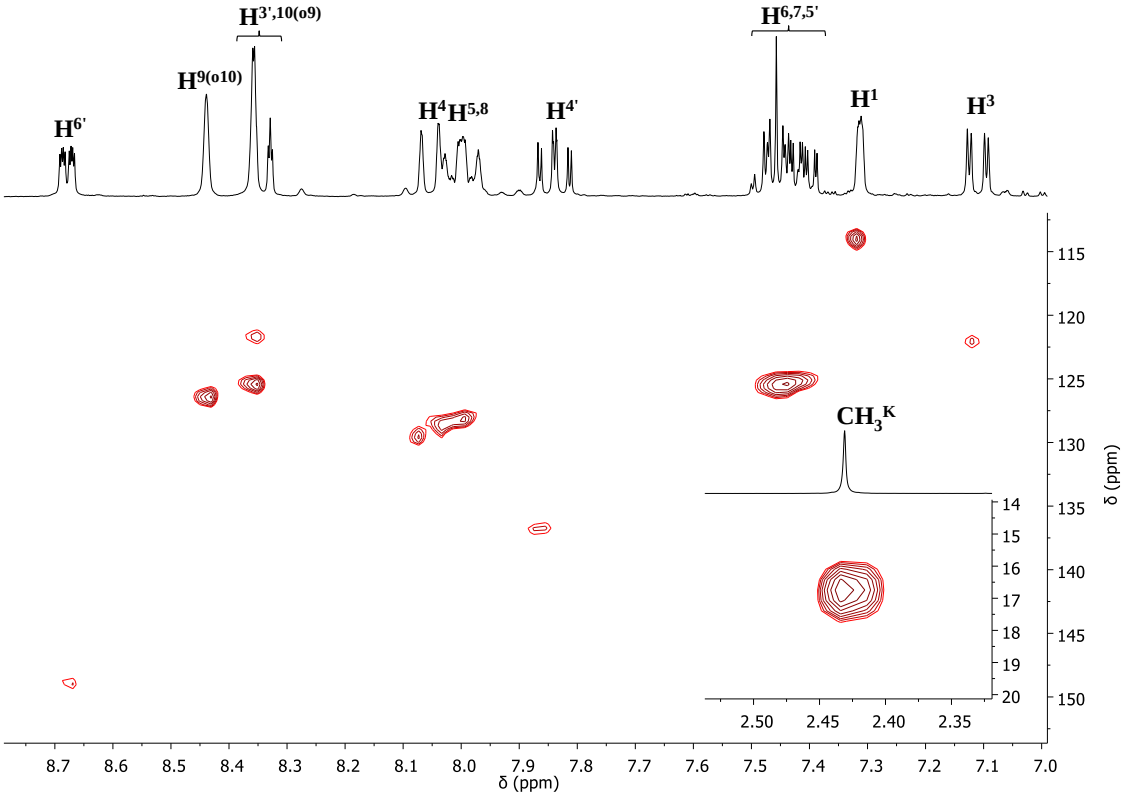

Figure S21. $^{1}H,^{13}C$ HSQC spectrum (CD_2Cl_2, 298 K) of ligand **8** (red = CH/CH_3).

NMR characterization of ligand 9 (CD_2Cl_2, T = 298 K)

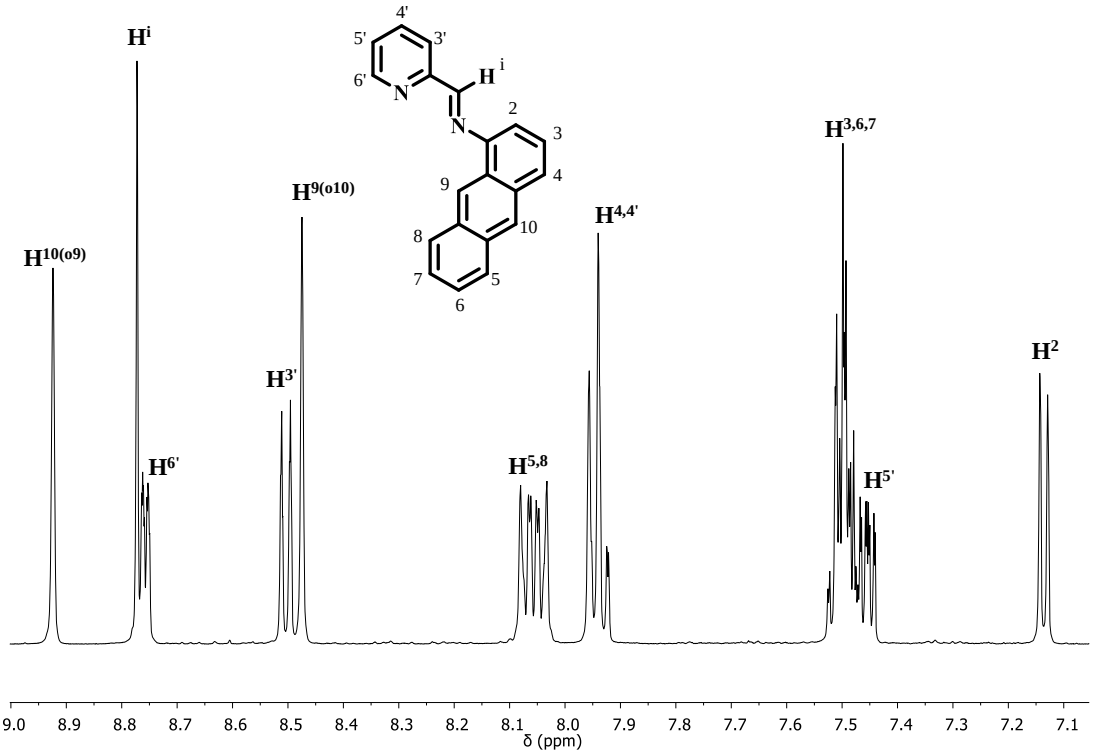

Figure S22. ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of ligand **9**.

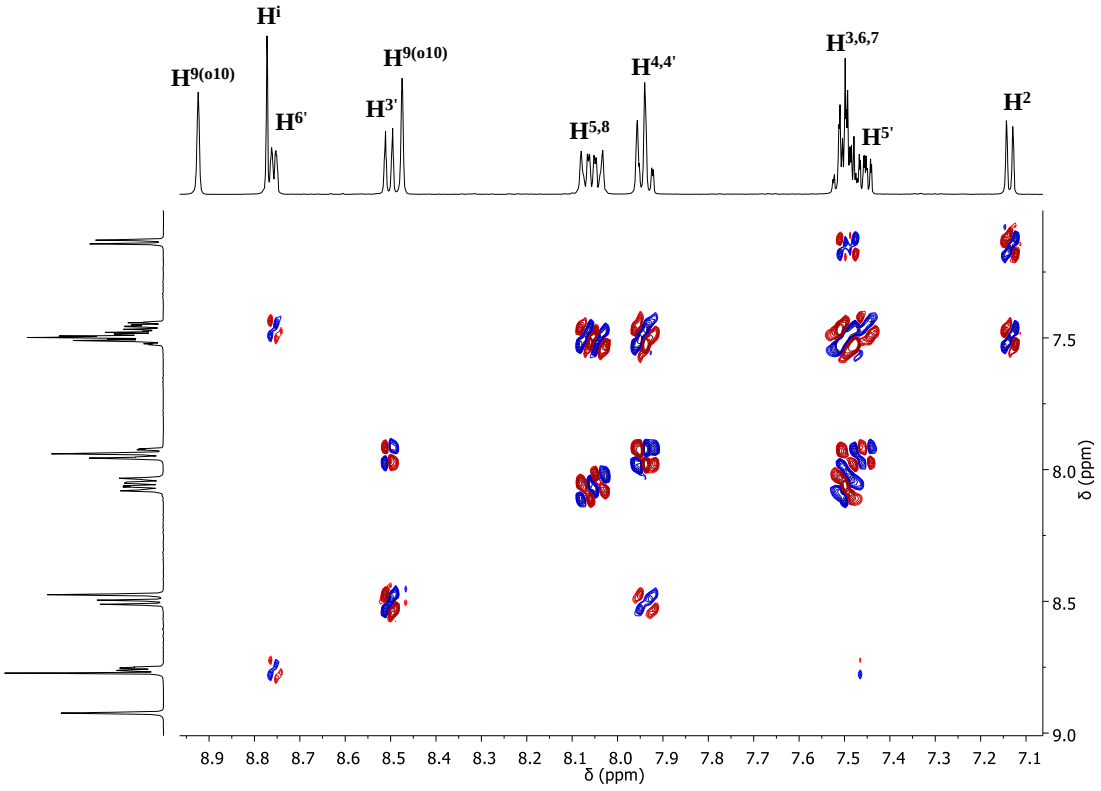

Figure S23. ^{1}H,^{1}H-DQCOSY spectrum (CD_2Cl_2, 298 K) of ligand **9**.

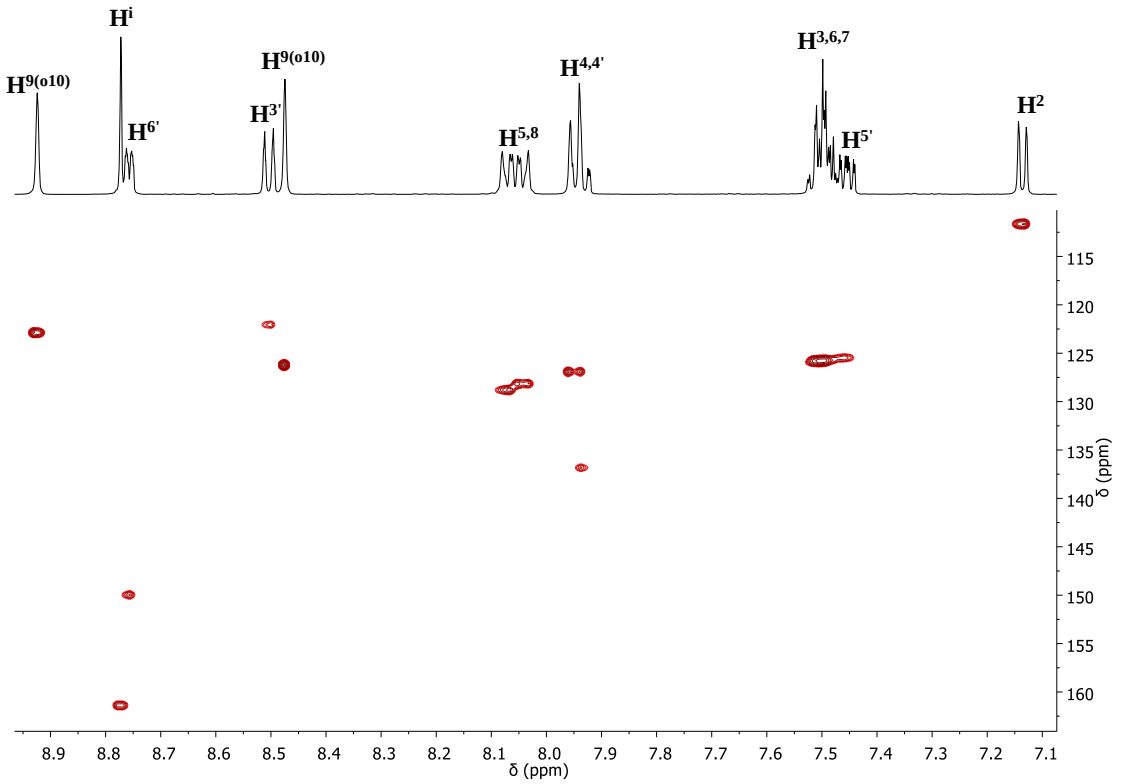

Figure S24. $^{1}H,^{13}C$-HSQC spectrum (CD_2Cl_2, 298 K) of ligand **9** (red = CH/CH_3).

NMR characterization of [Pd(CH_3)Cl(1)] 1a (CD_2Cl_2, T = 298 K)

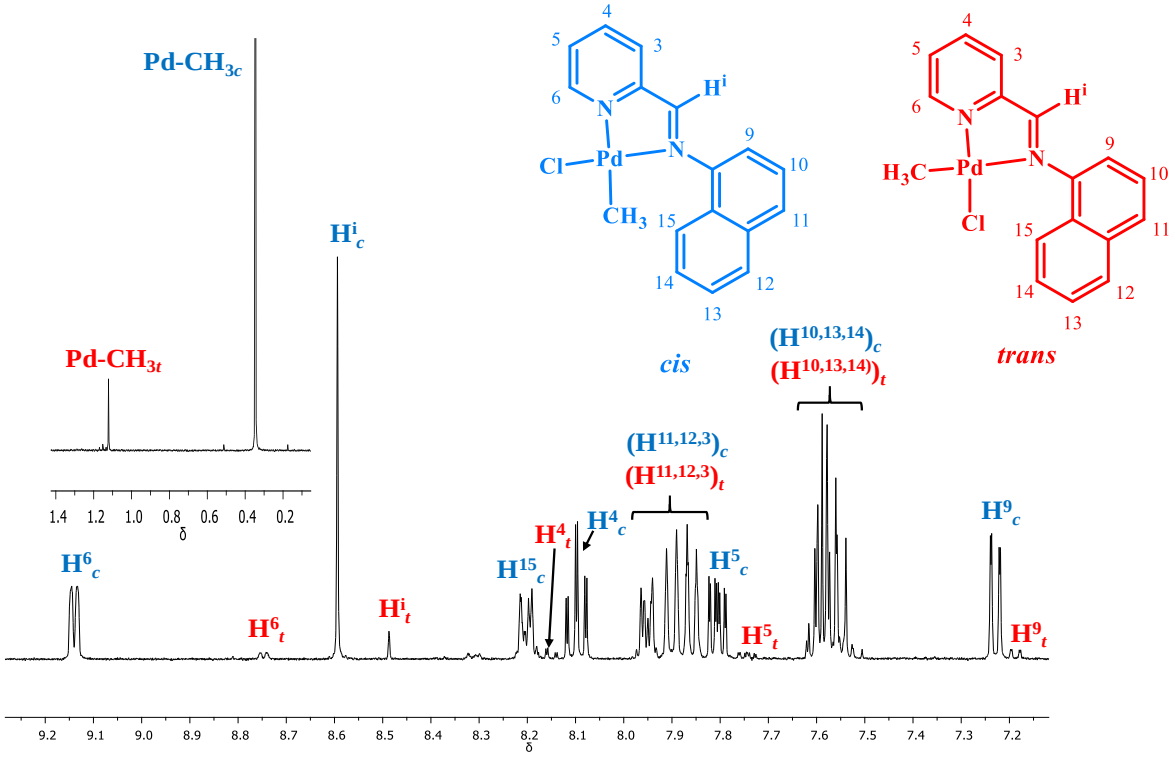

Figure S25. ^{1}H NMR spectrum (CD_2Cl_2, T= 298 K) of complex **1a** (aromatic and aliphatic region not on scale).

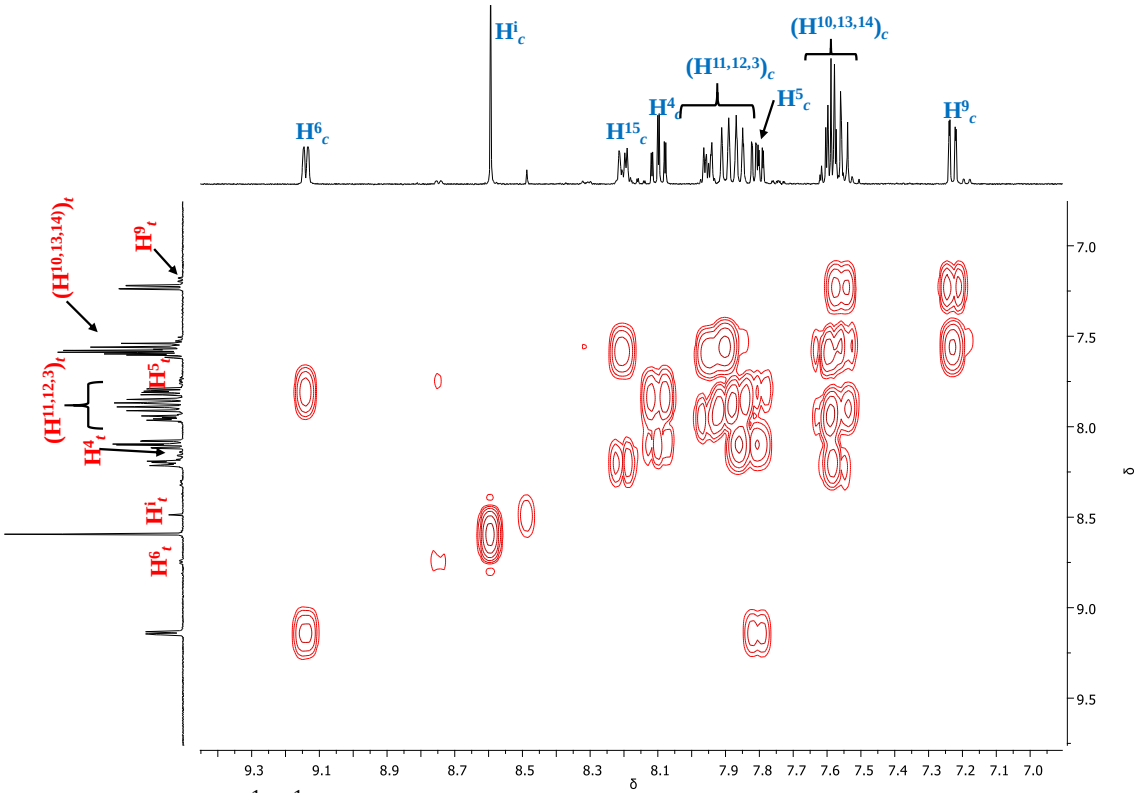

Figure S26. ^{1}H,^{1}H-COSY spectrum (CD_2Cl_2, T= 298 K) of **1a**, aromatic region.

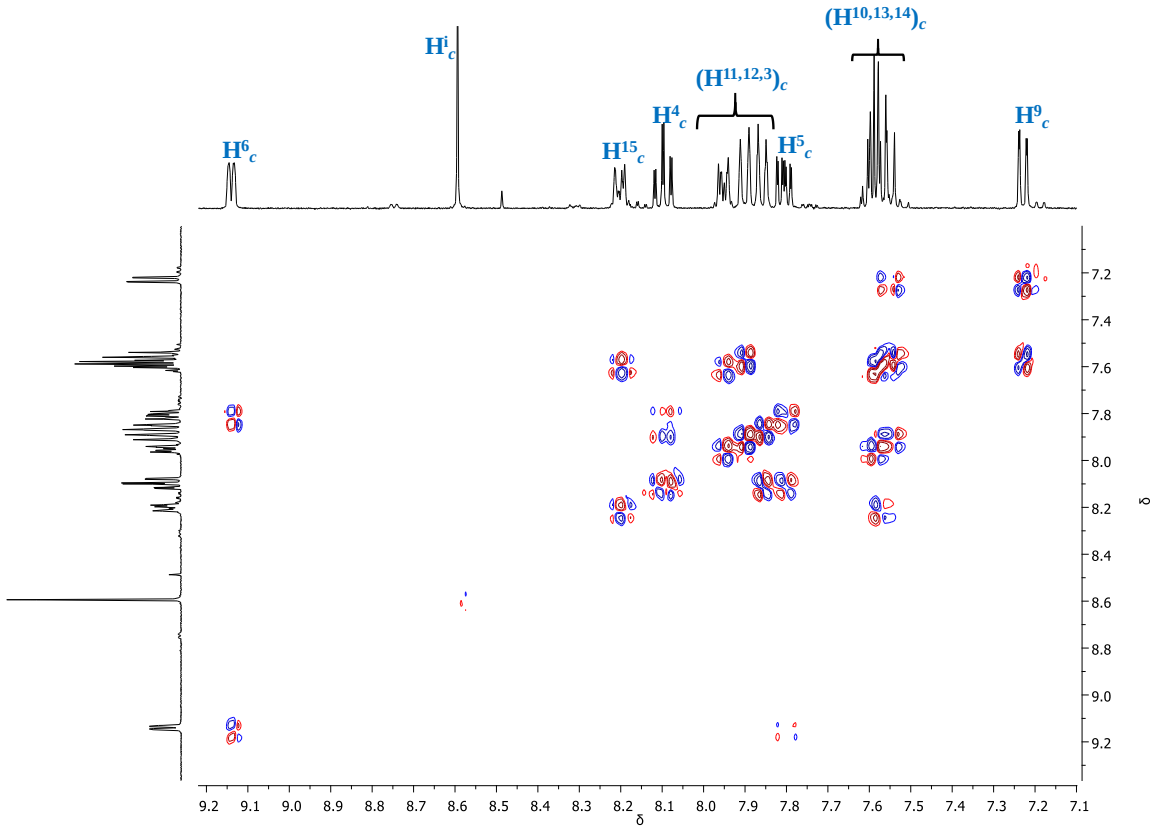

Figure S27. ^{1}H,^{1}H-DQCOSY spectrum (CD_2Cl_2, T= 298 K) of **1a**, aromatic region.

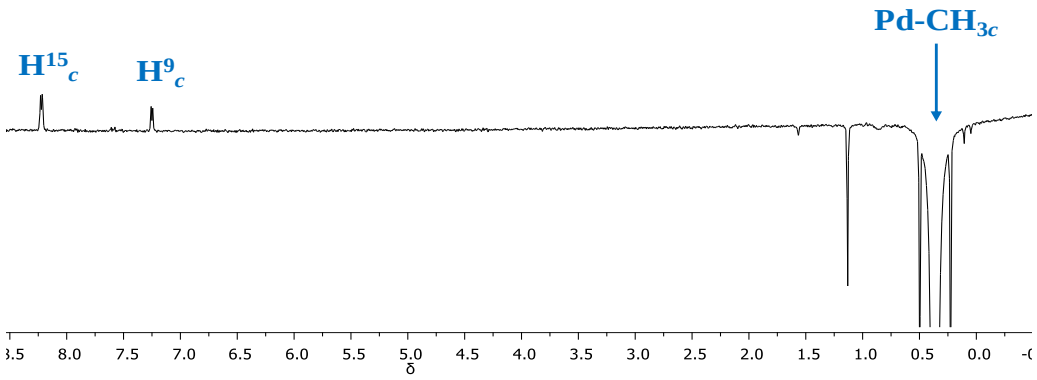

Figure S28. NOESY1D spectrum (CD_2Cl_2, T= 298 K) of **1a**: irradiated singlet at 0.35 ppm.

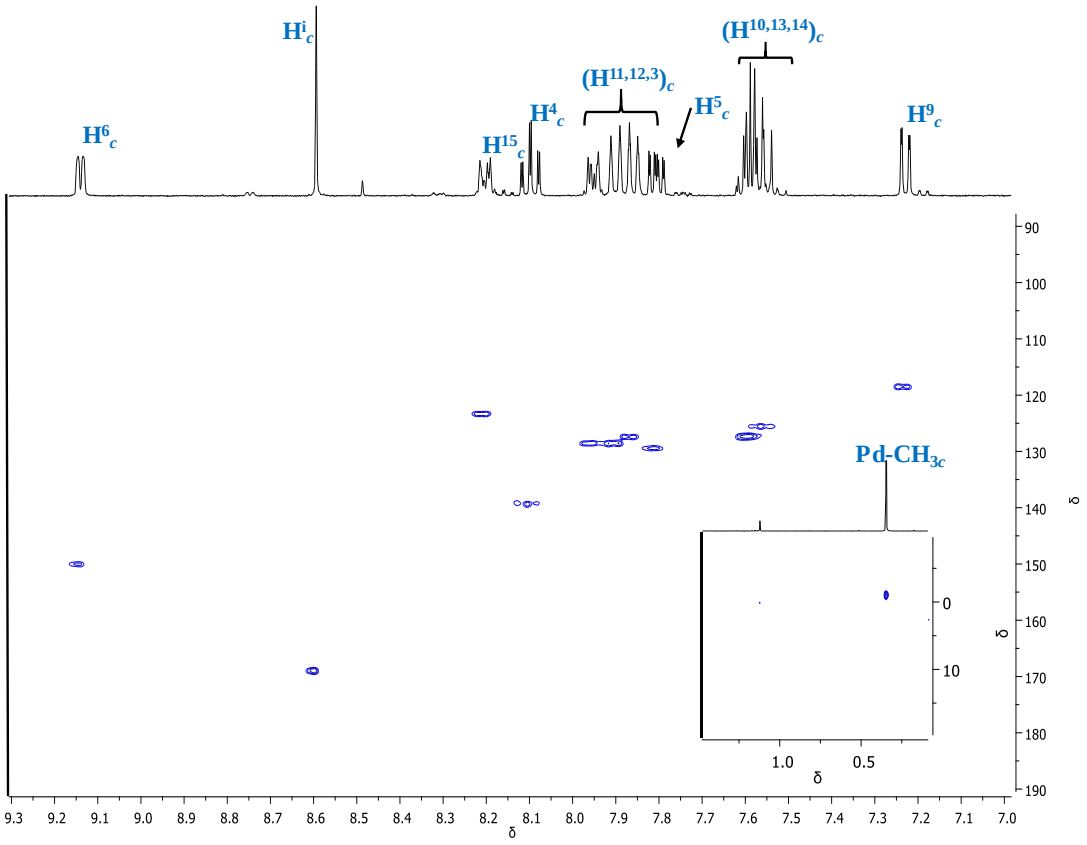

Figure S29. $^{1}H,^{13}C$-HSQC spectrum (CD_2Cl_2, T= 298 K) of **1a** (blue = CH/CH_3).

NMR characterization of [Pd(CH_3)Cl(2)] 2a (CD_2Cl_2, T = 298 K)

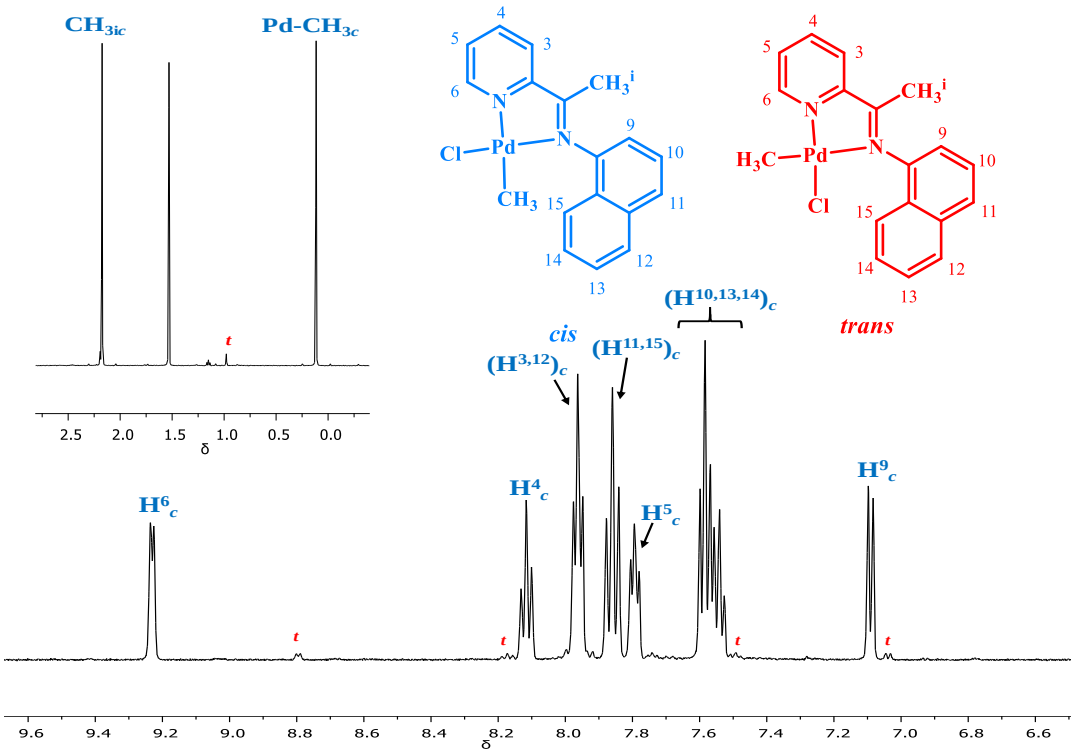

Figure S30. ^{1}H NMR spectrum (CD_2Cl_2, T= 298 K) of **2a** (aromatic and aliphatic region not on scale).

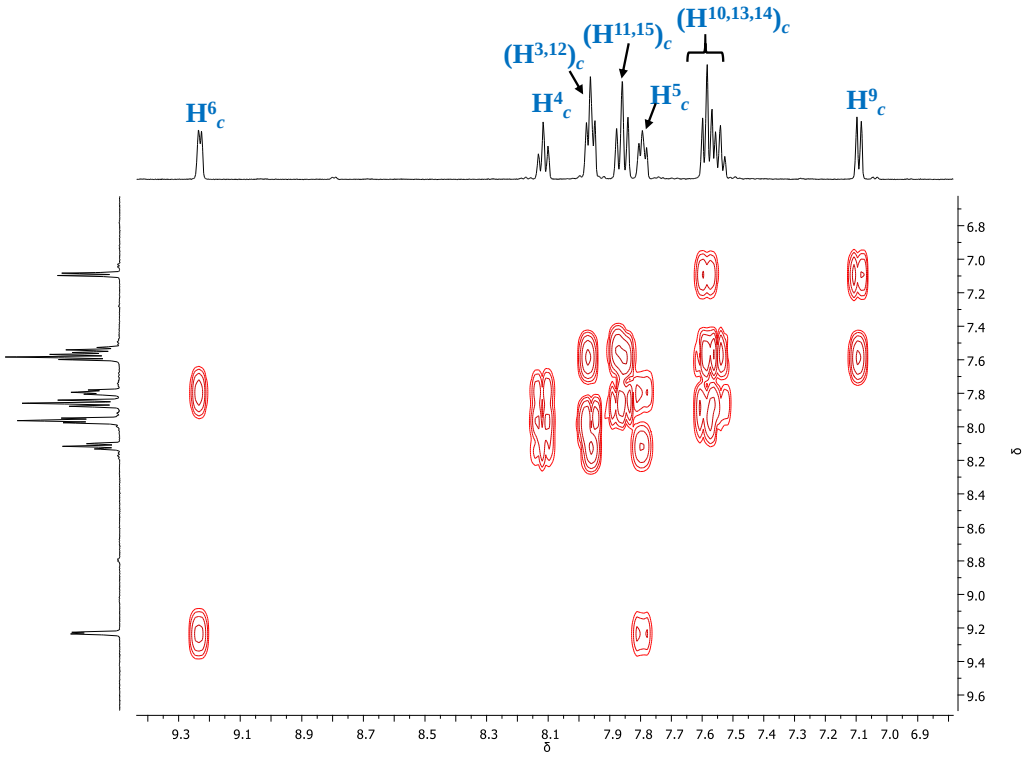

Figure S31. ^{1}H,^{1}H-COSY spectrum (CD_2Cl_2, T= 298 K) of complex **2a**, aromatic region.

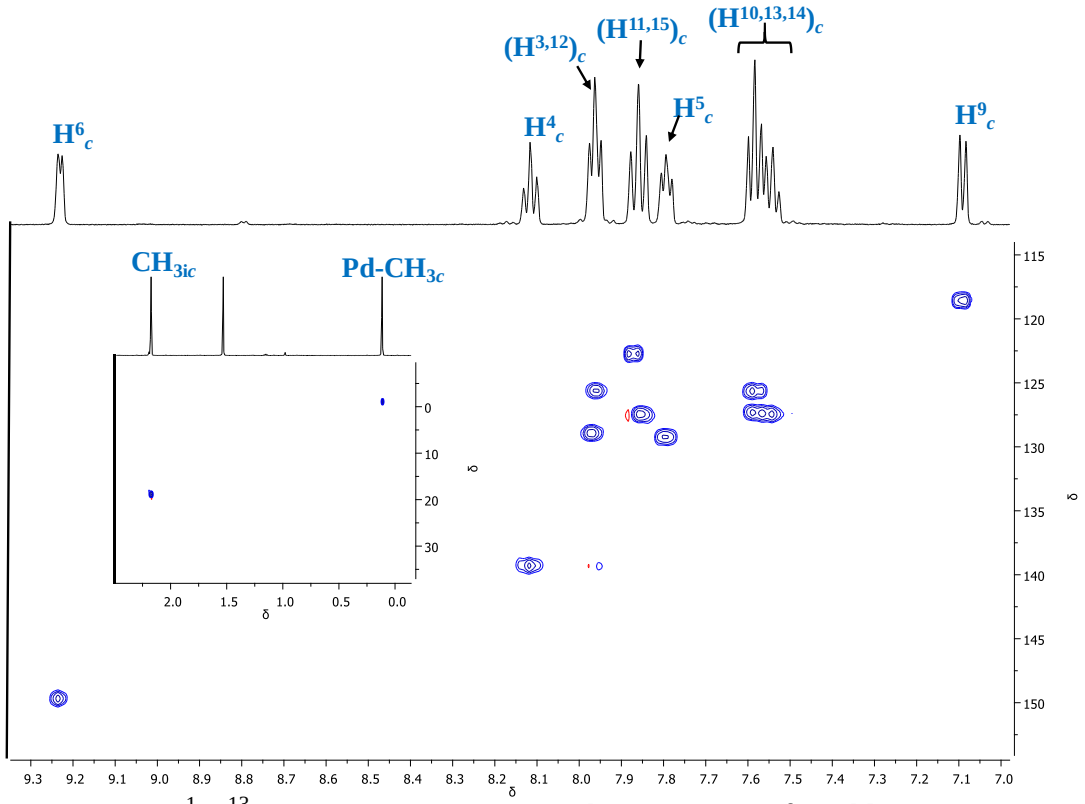

Figure S32. $^{1}H,^{13}C$-HSQC spectrum (CD_2Cl_2, T= 298 K) of **2a** (blue = CH/CH_3).

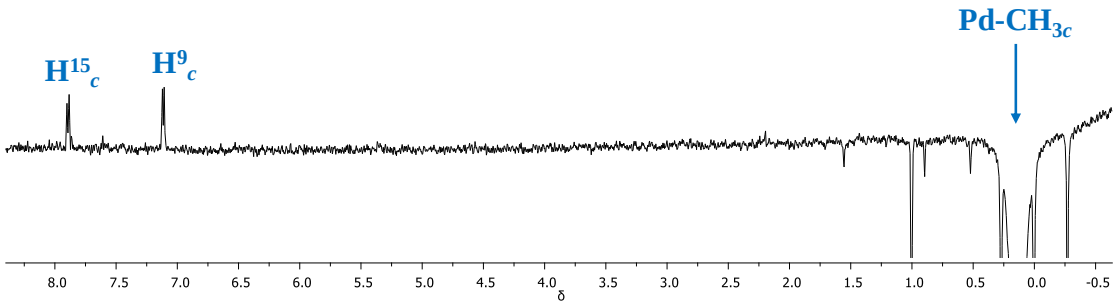

Figure S33. NOESY1D spectrum (CD_2Cl_2, T= 298 K) of **2a**: irradiated signal at 0.11 ppm.

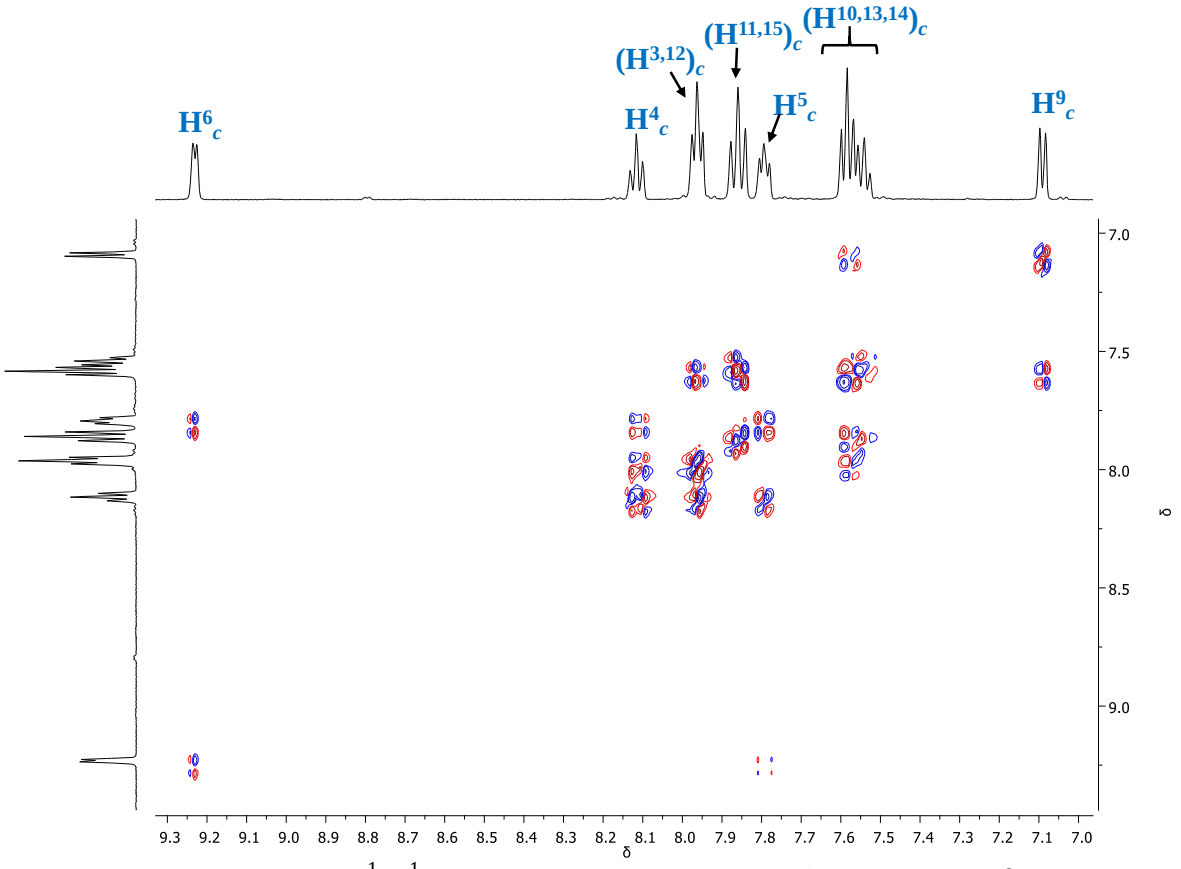

Figure S34. ^{1}H,^{1}H-DQCOSY spectrum (CD_2Cl_2, T= 298 K) of **2a**.

NMR characterization of [Pd(CH$_3$)Cl(3)] 3a (CD_2Cl_2, T = 273 K)

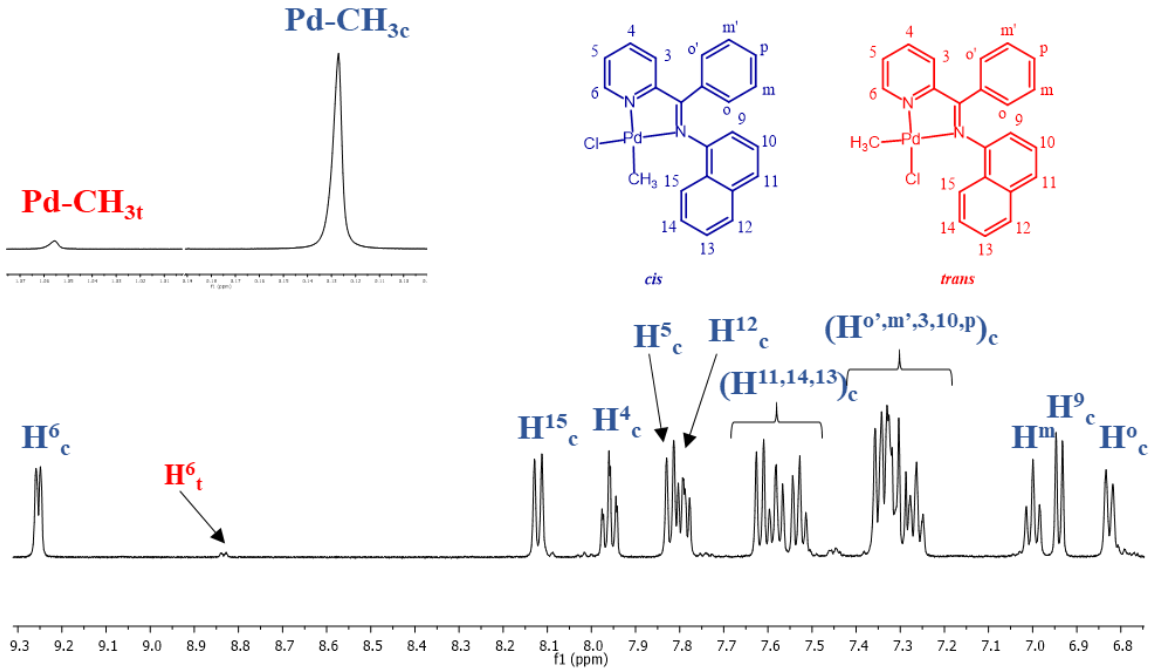

Figure S35. ^{1}H NMR spectrum (CD_2Cl_2, T = 273 K) of complex **3a**.

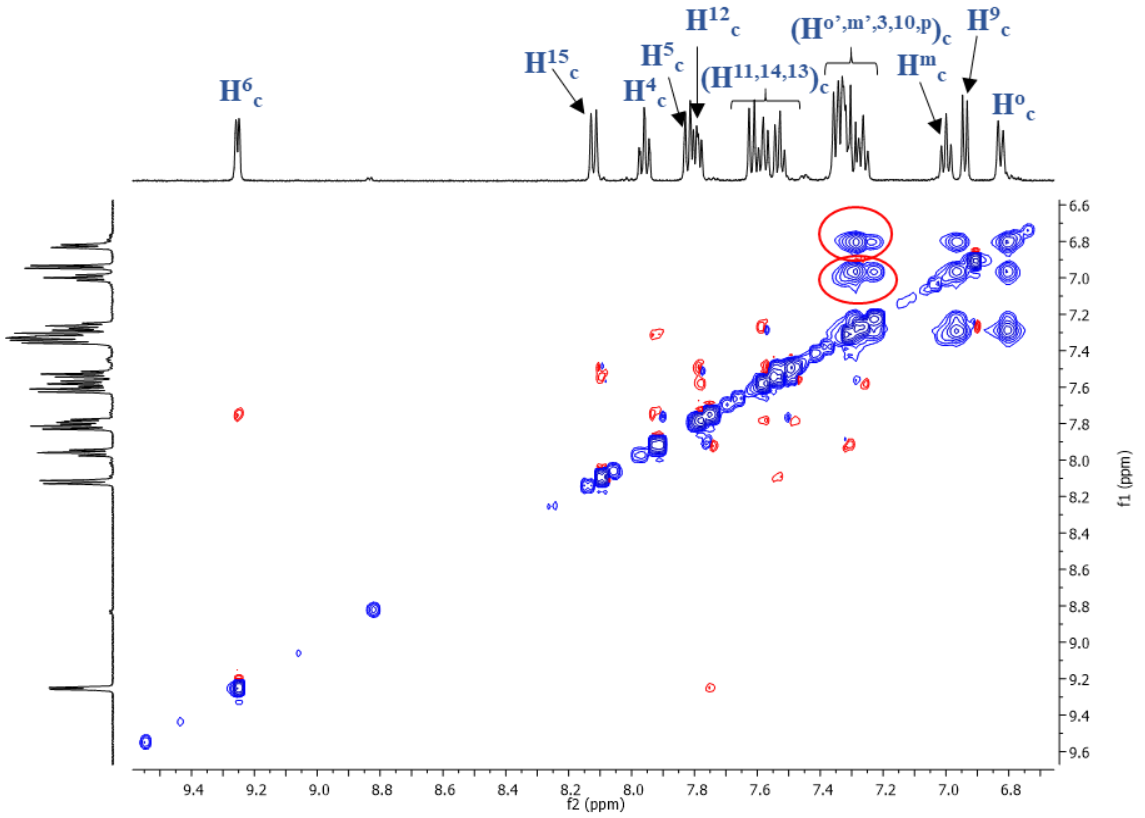

Figure S36. ^{1}H,^{1}H-NOESYspectrum (CD_2Cl_2, T = 273 K) of **3a** (exchange peaks circled in red).

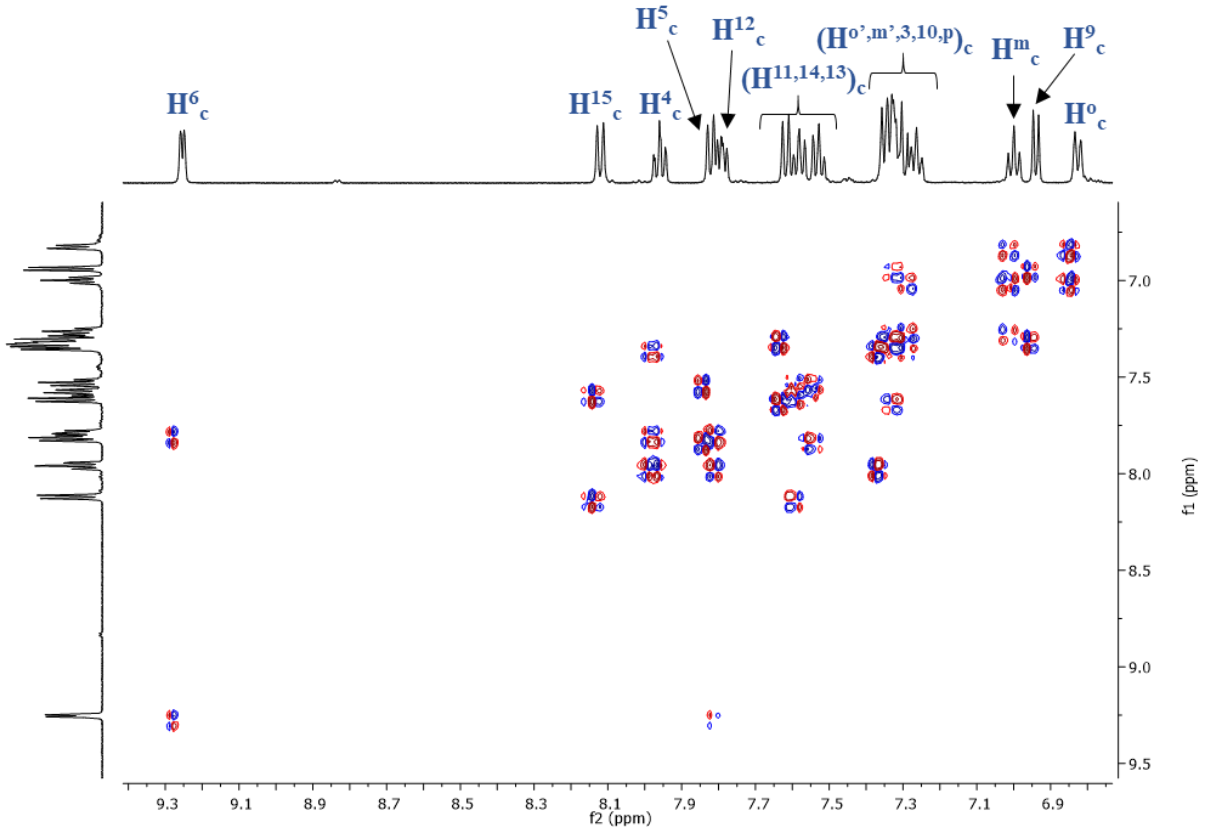

Figure S37. ^{1}H,^{1}H-DQCOSY spectrum (CD_2Cl_2, T = 273 K) of complex **3a**.

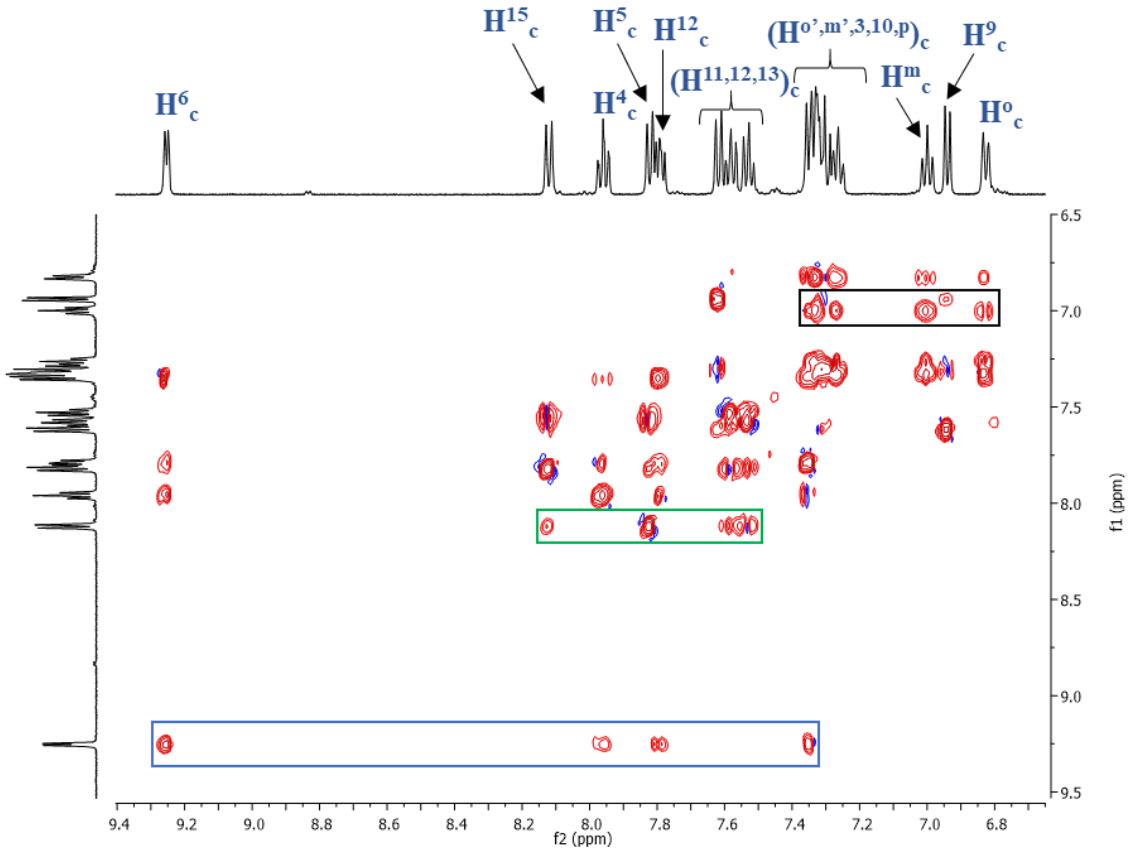

Figure S38. ^{1}H,^{1}H-TOCSY spectrum (CD_2Cl_2, T = 273 K) of **3a**. (Signals of the phenyl group: black rectangle; naphthyl: green rectangle; pyridine: blue rectangle).

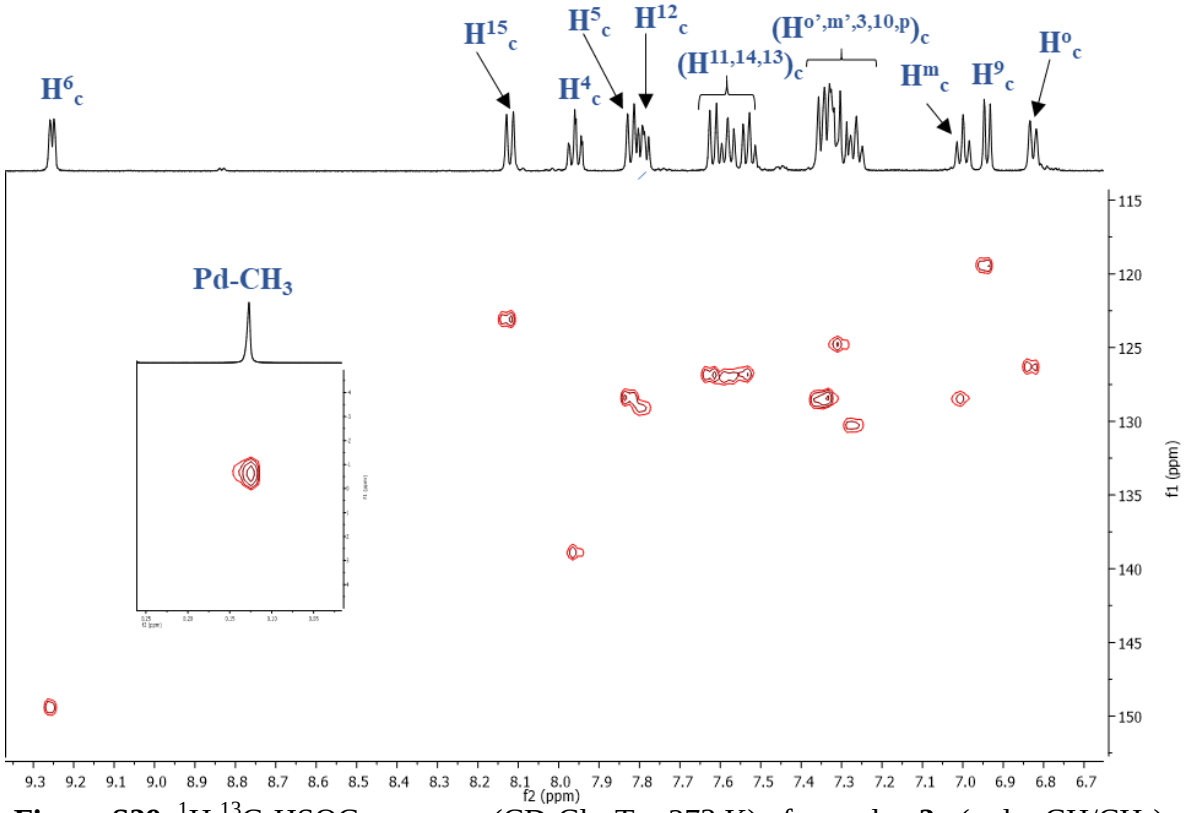

Figure S39. ^{1}H,^{13}C-HSQC spectrum (CD_2Cl_2, T = 273 K) of complex **3a** (red = CH/CH_3).

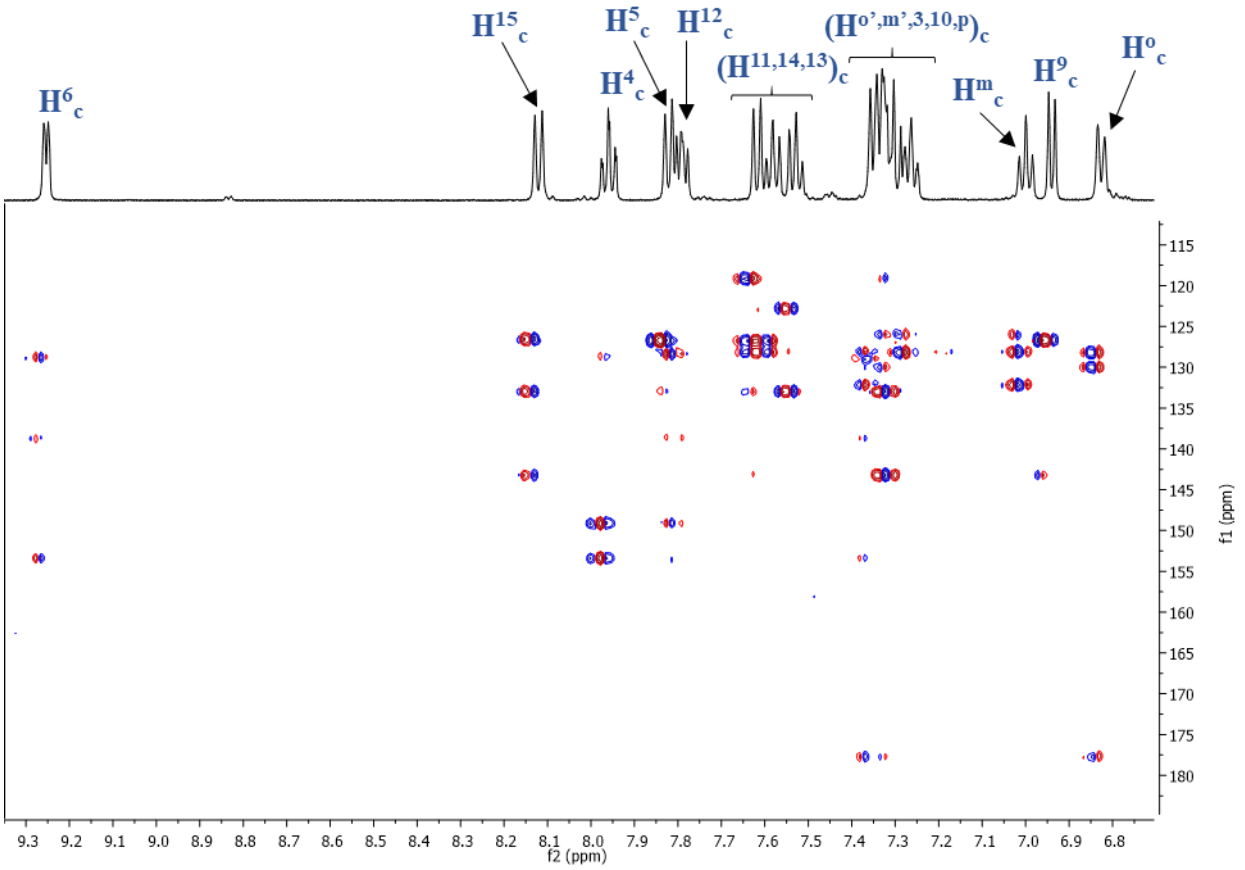

Figure S40. $^{1}H,^{13}C$-HMBC spectrum (CD_2Cl_2, T = 273 K) of **3a**.

NMR characterization of [Pd(CH$_3$)Cl(4)] 4a (CD_2Cl_2, T = 298 K)

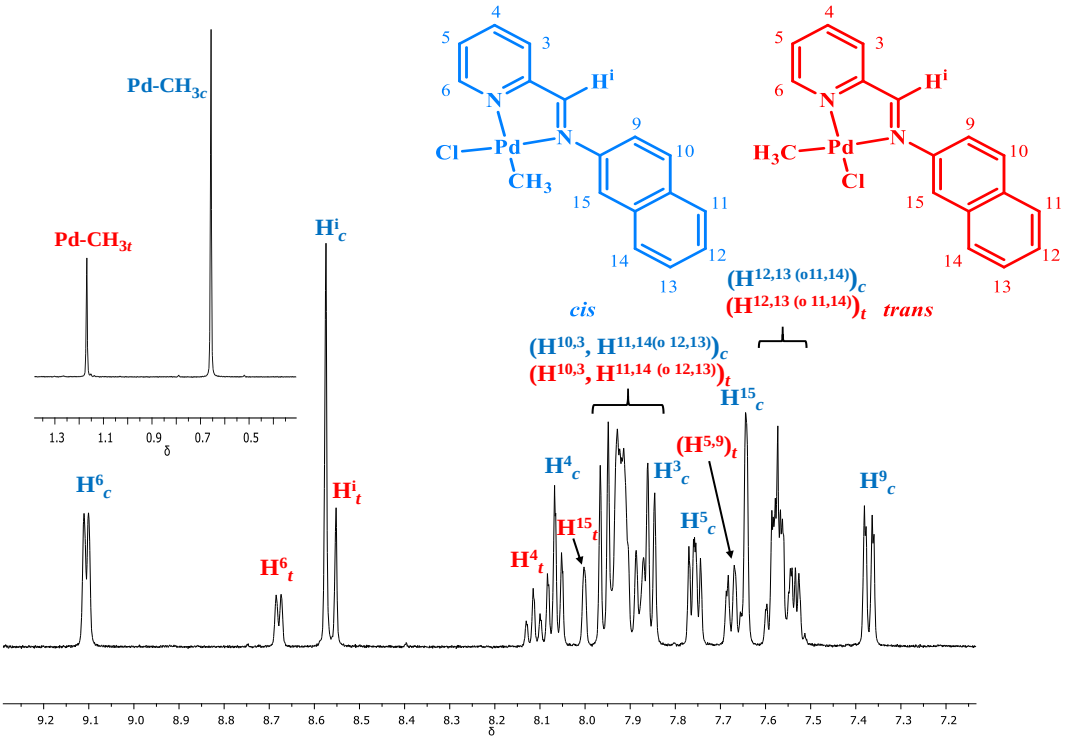

Figure S41. ^{1}H NMR spectrum (CD_2Cl_2, T= 298 K) of **4a** (aromatic and aliphatic region not on scale).

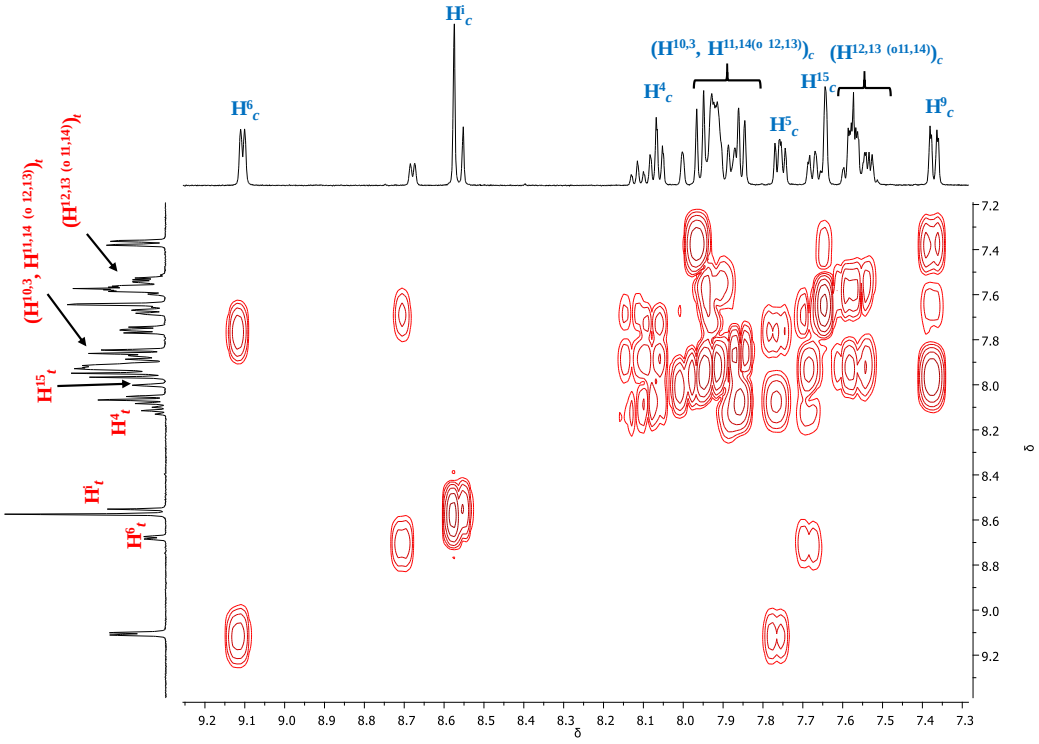

Figure S42. $^{1}H,^{1}H$-COSY spectrum (CD_2Cl_2, T= 298 K) of **4a**.

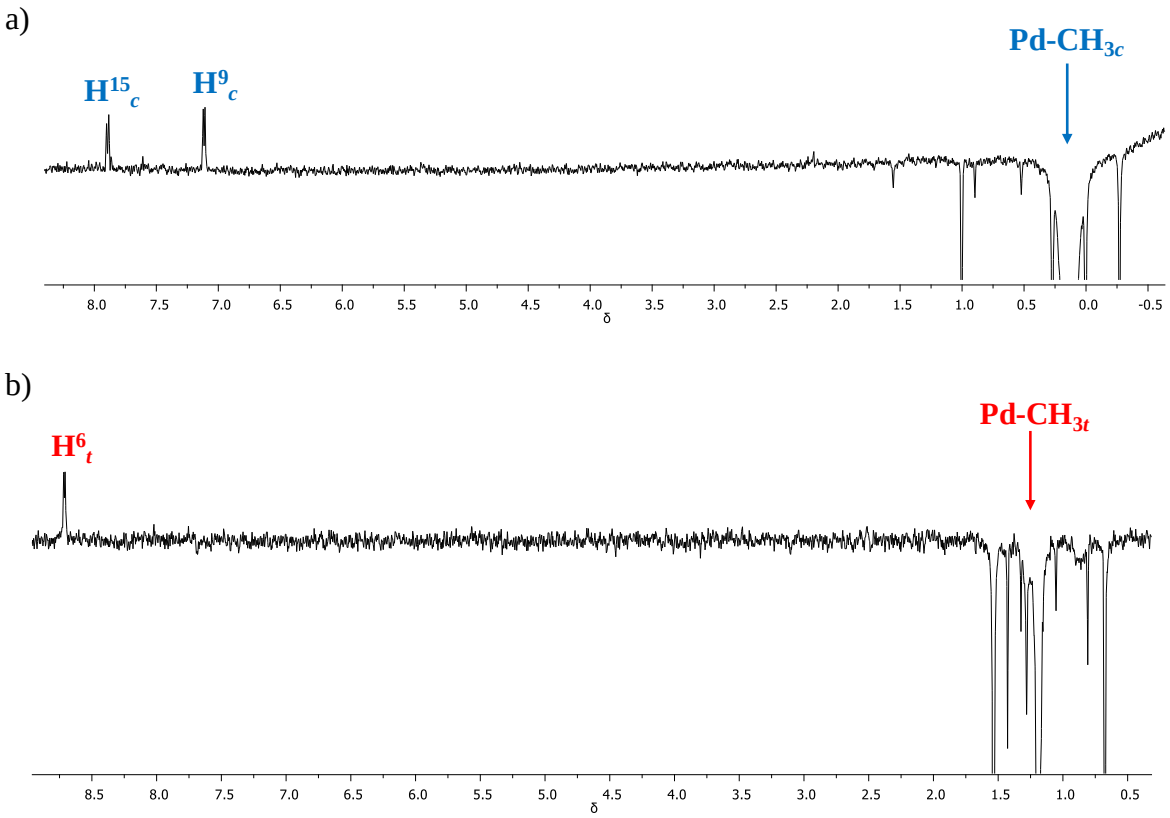

Figure S43. NOESY1D spectra (CD_2Cl_2, T= 298 K) of **4a**: a) irradiated signal at 0.66 ppm; b) irradiated signal at 1.17 ppm.

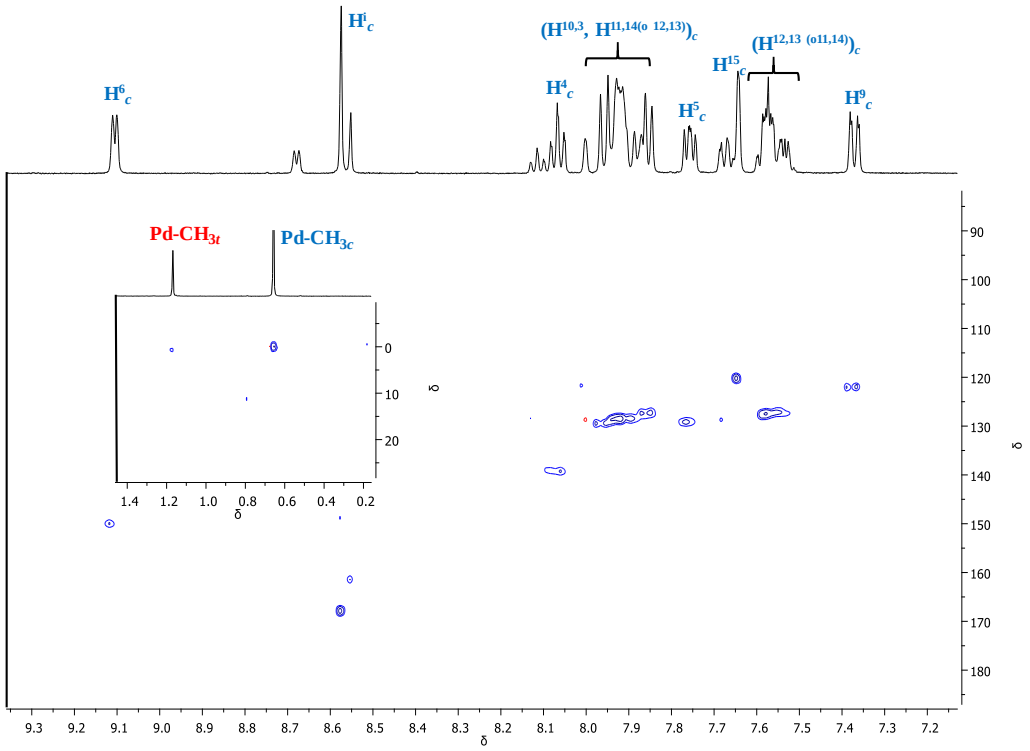

Figure S44. $^{1}H,^{13}C$-HSQC spectrum (CD_2Cl_2, T= 298 K) of **4a** (blue = CH/CH_3).

NMR characterization of [Pd(CH_3)Cl(5)] 5a (CD_2Cl_2, T = 298 K)

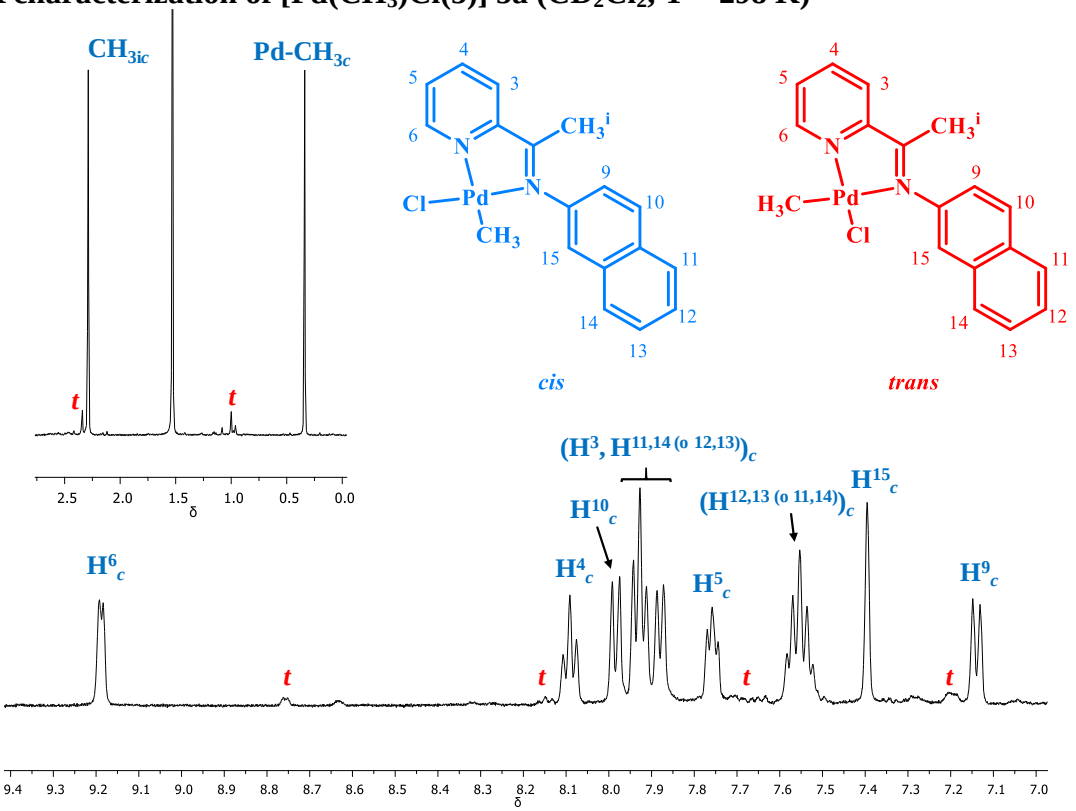

Figure S45. ^{1}H NMR spectrum (CD_2Cl_2, T= 298 K) of **5a** (aromatic and aliphatic region not on scale).

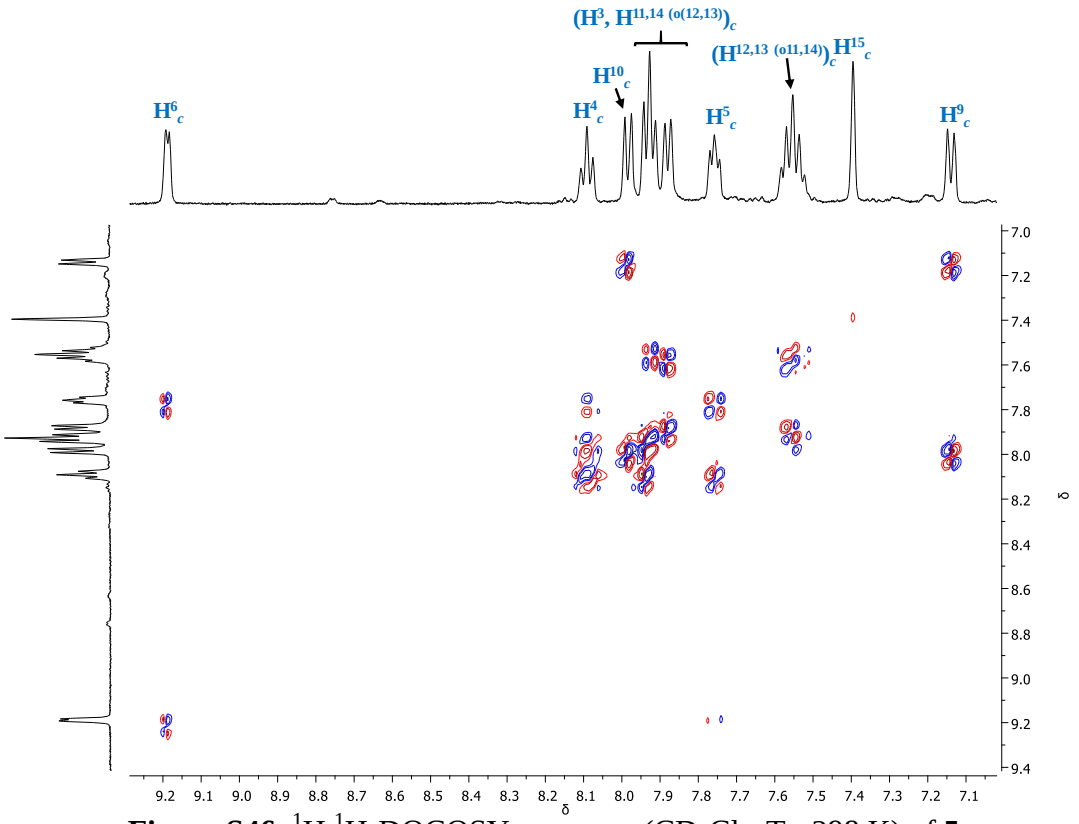

Figure S46. ^{1}H,^{1}H-DQCOSY spectrum (CD_2Cl_2, T= 298 K) of **5a**.

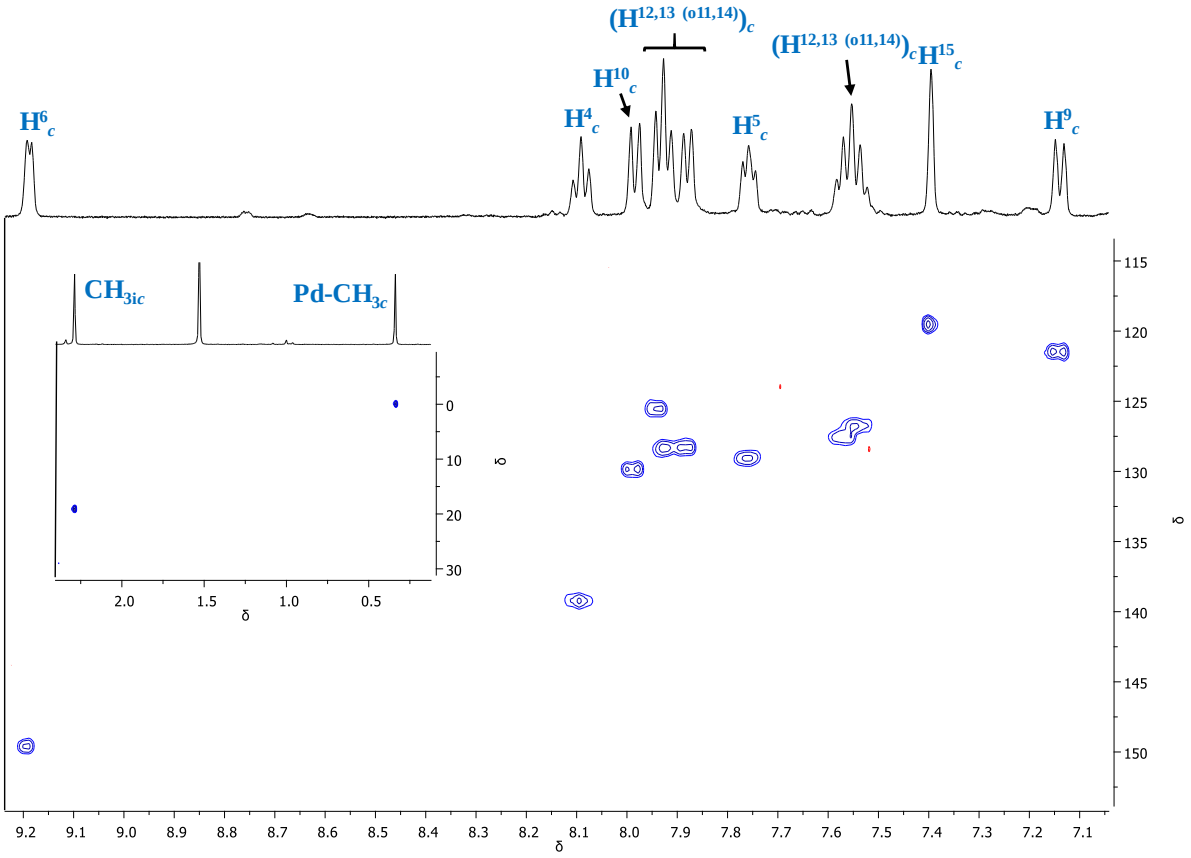

Figure S47. ^{1}H,^{13}C-HSQC spectrum (CD_2Cl_2, T= 298 K) of **5a** (blue = CH/CH_3).

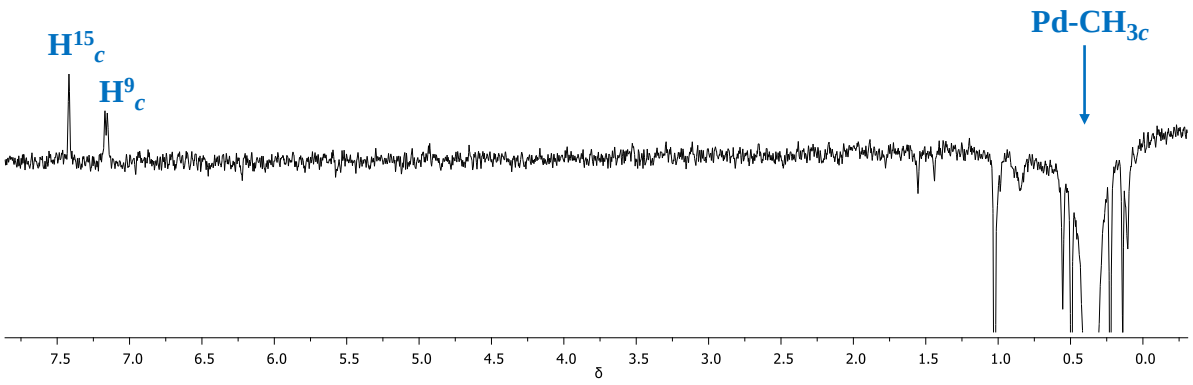

Figure S48. NOESY1D spectrum (CD_2Cl_2, T= 298 K) of **5a**, irradiated signal at 0.34 ppm.

NMR characterization of [Pd(CH_3)Cl(6)] 6a (CD_2Cl_2, T = 298 K)

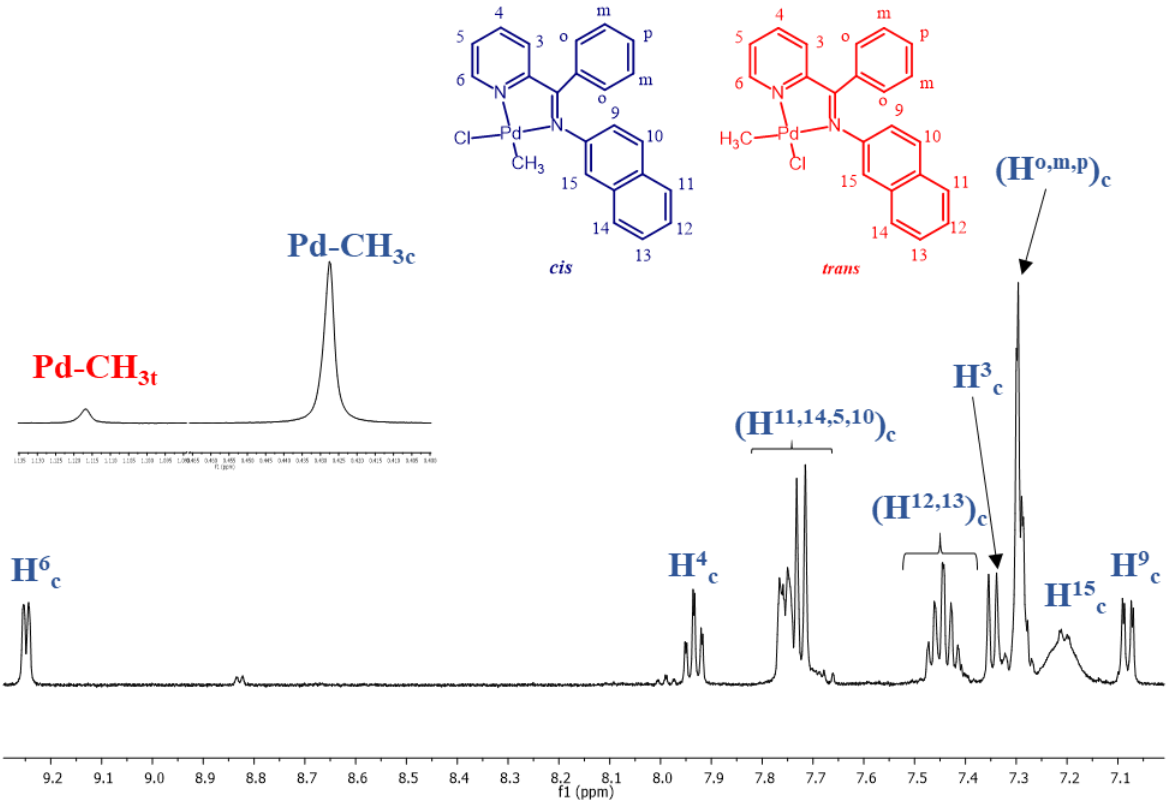

Figure S49. ^{1}H NMR spectrum (CD_2Cl_2, T = 298 K) of **6a**.

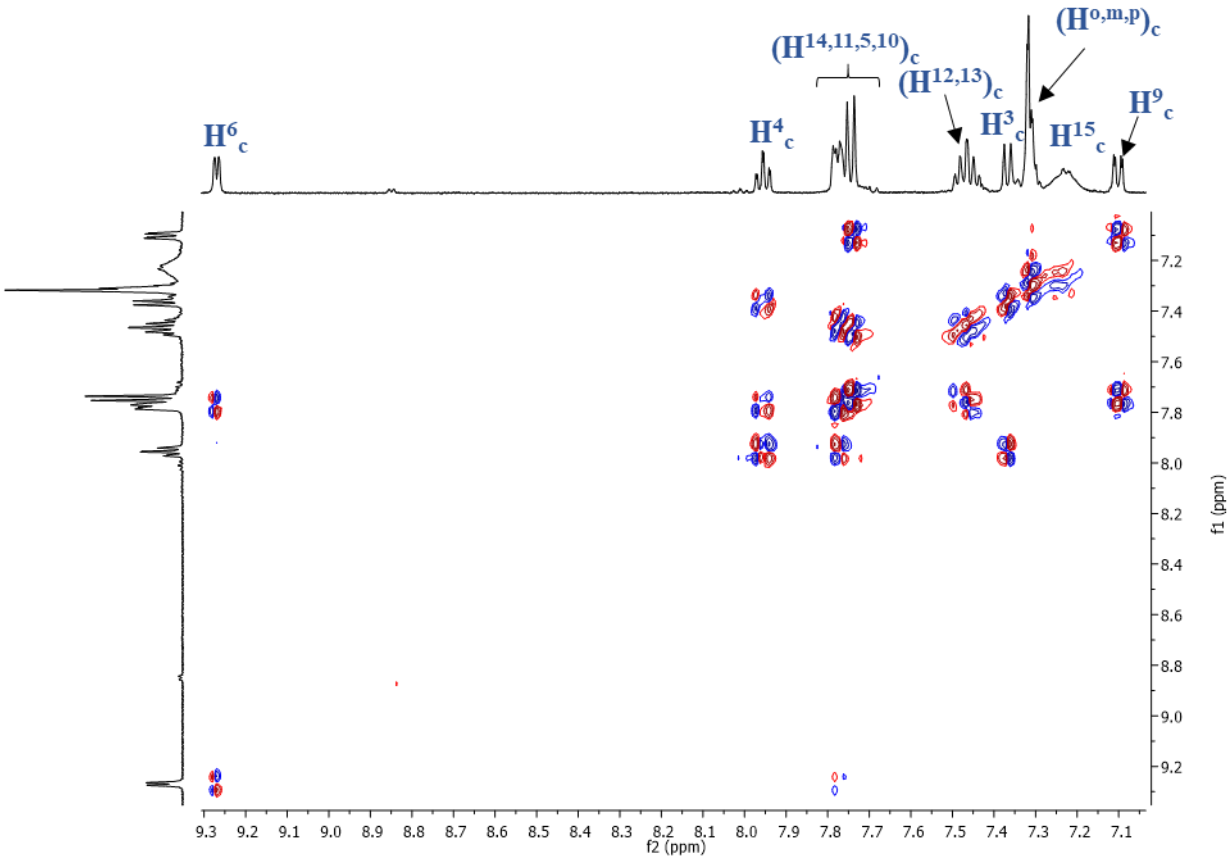

Figure S50. ^{1}H,^{1}H-DQCOSY spectrum (CD_2Cl_2, T = 298 K) of **6a**, aromatic region.

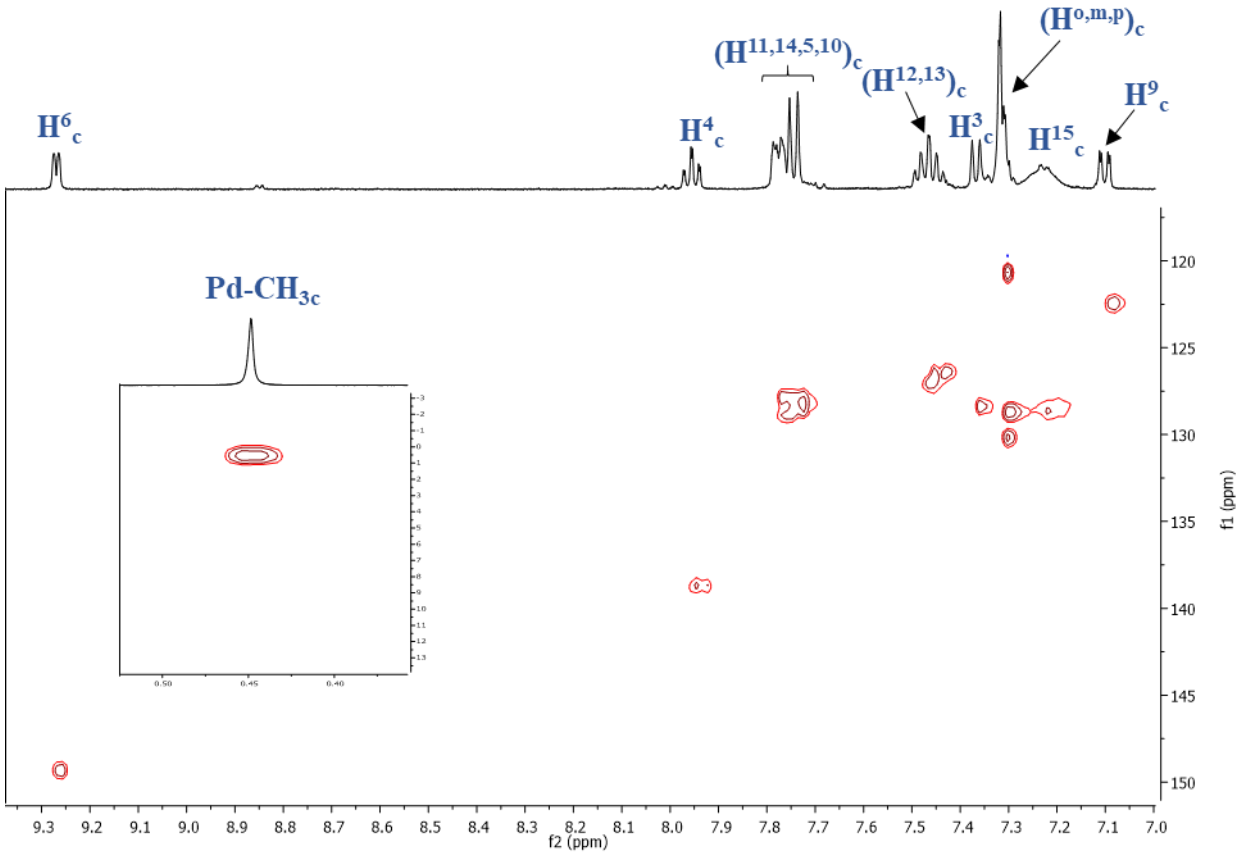

Figure S51. ^{1}H,^{13}C-HSQC spectrum (CD_2Cl_2, T = 298 K) of **6a**; red = CH/CH_3.

NMR characterization of [Pd(CH$_3$)Cl(7)] 7a (CD$_2$Cl$_2$, T = 298 K)

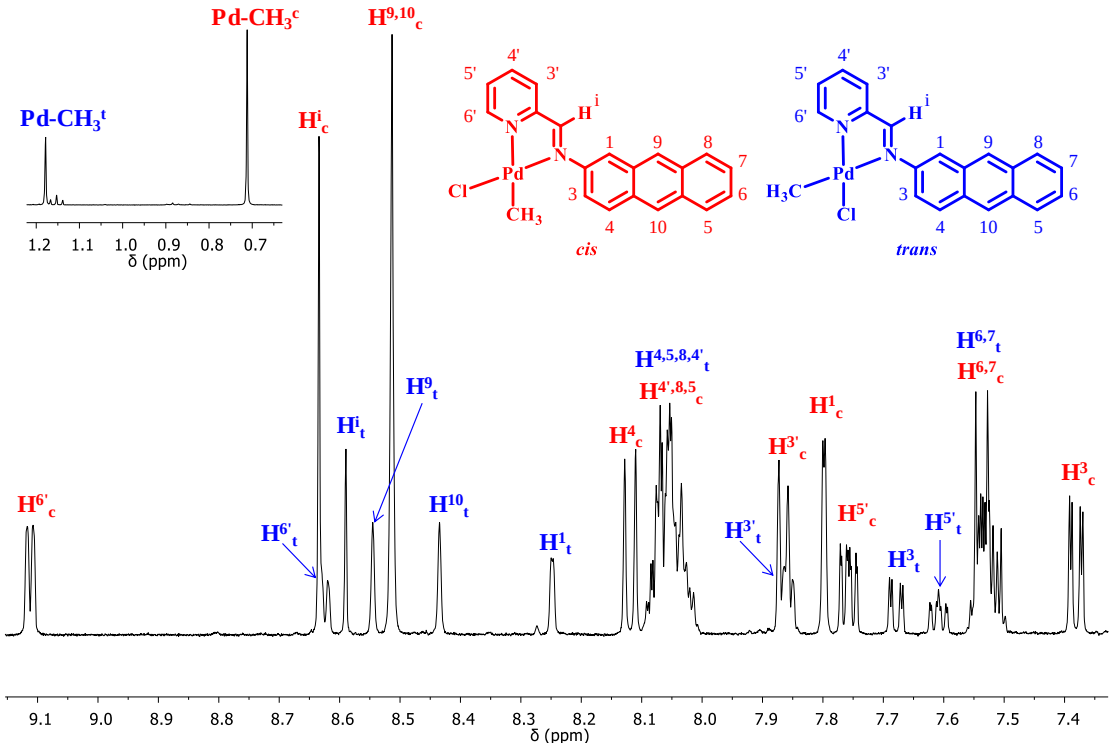

Figure S52. ^{1}H–NMR spectrum (CD$_2$Cl$_2$, 298 K) of **7a**.

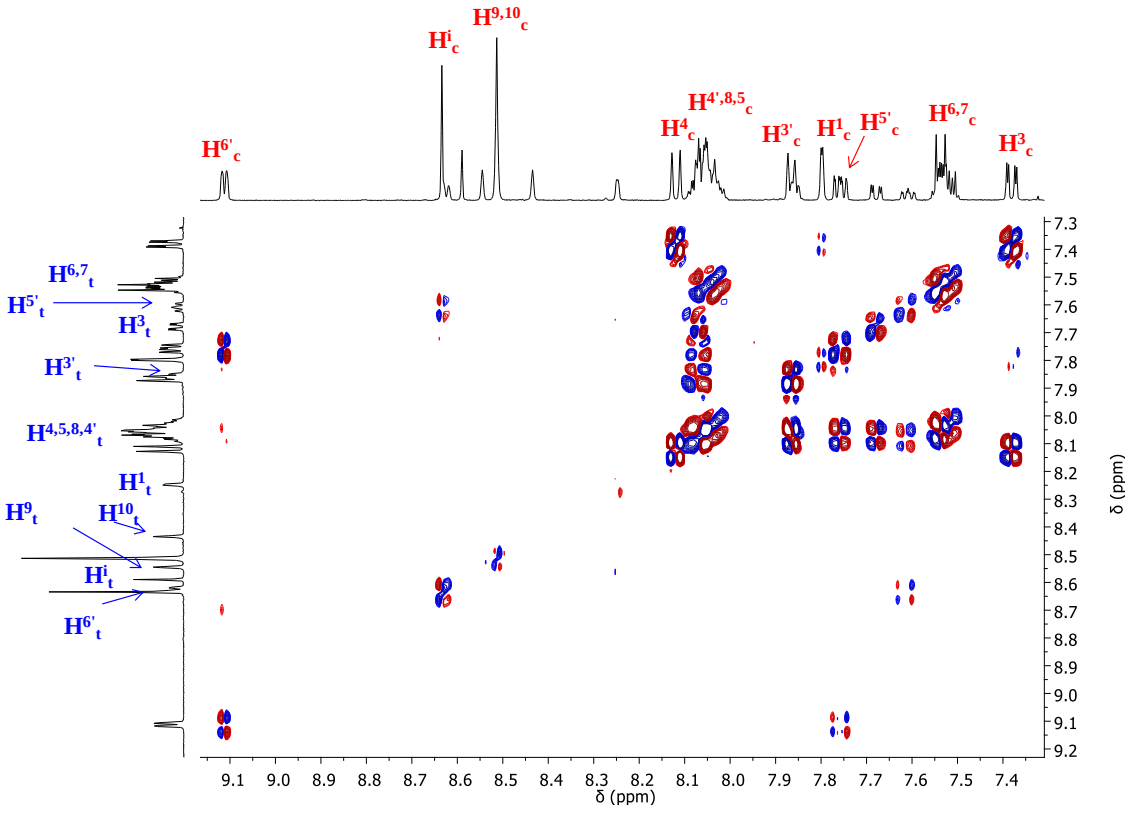

Figure S53. ^{1}H,^{1}H–DQCOSY (CD$_2$Cl$_2$, 298 K) of **7a**, aromatic region.

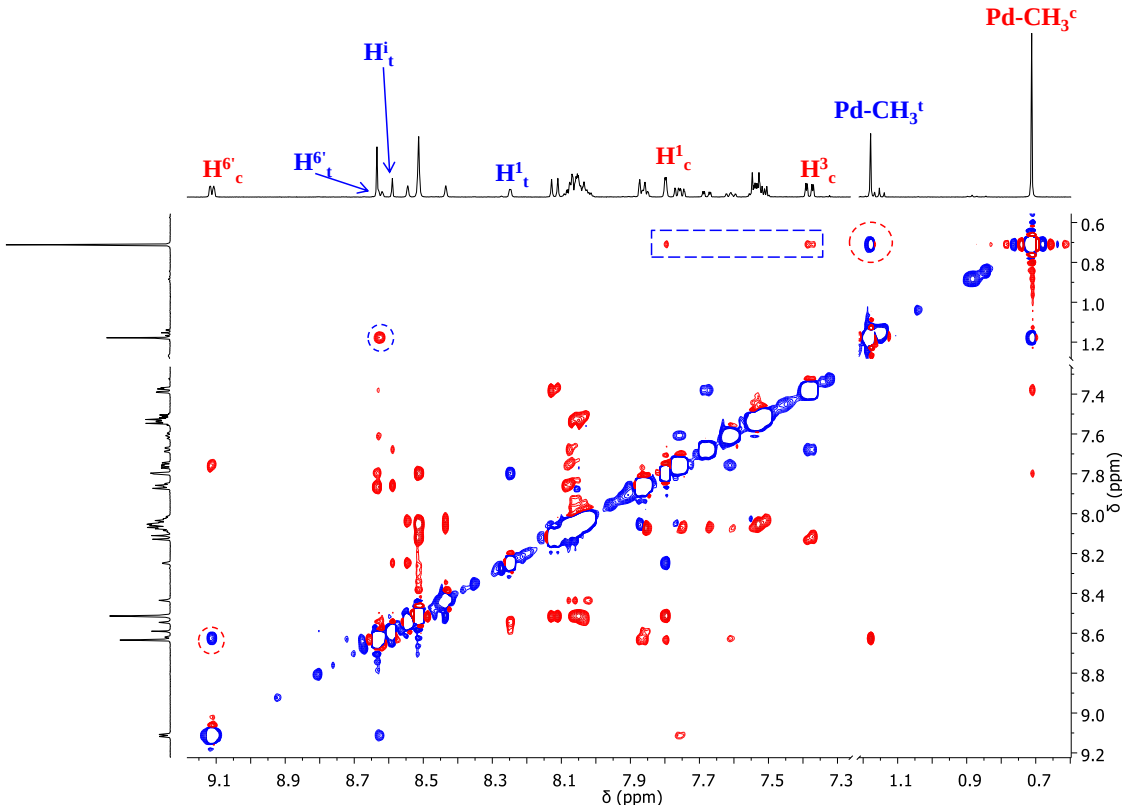

Figure S54. ^{1}H,^{1}H–NOESY spectrum (CD_2Cl_2, 298 K) of **7a** (blue = exchange peaks, red = NOE peaks).

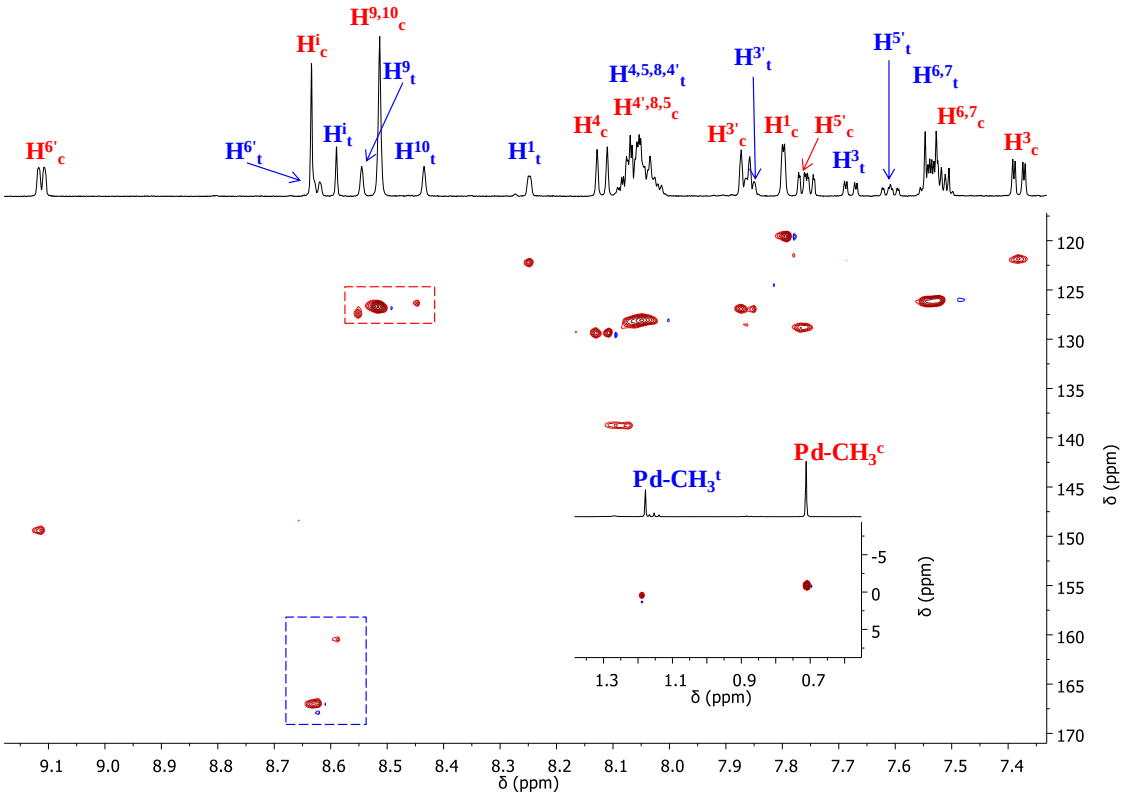

Figure S55. ^{1}H,^{13}C–HSQC spectrum (CD_2Cl_2, 298 K) of **7a** (red = CH/CH_3).

NMR characterization of [Pd(CH_3)Cl(8)] 8a (CD_2Cl_2, T = 298 K)

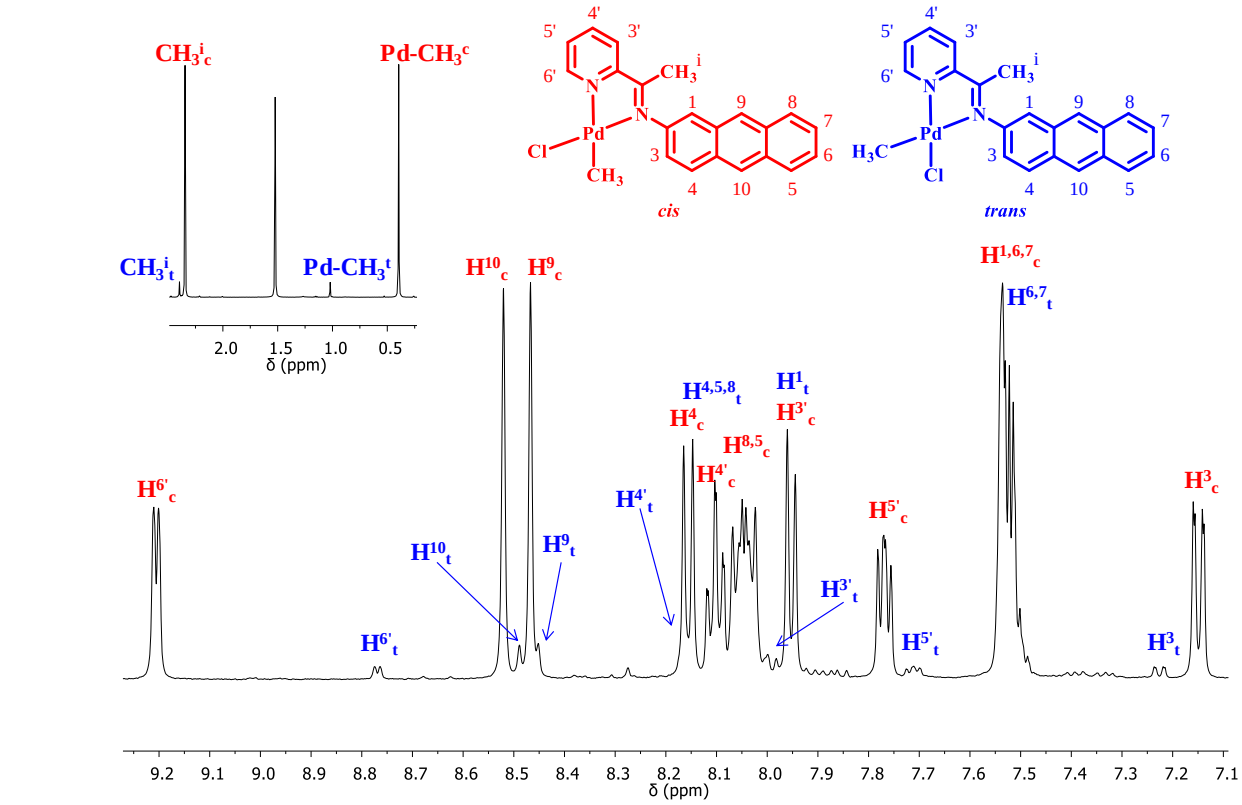

Figure S56. ^{1}H–NMR spectrum (CD_2Cl_2, 298 K) of **8a**.

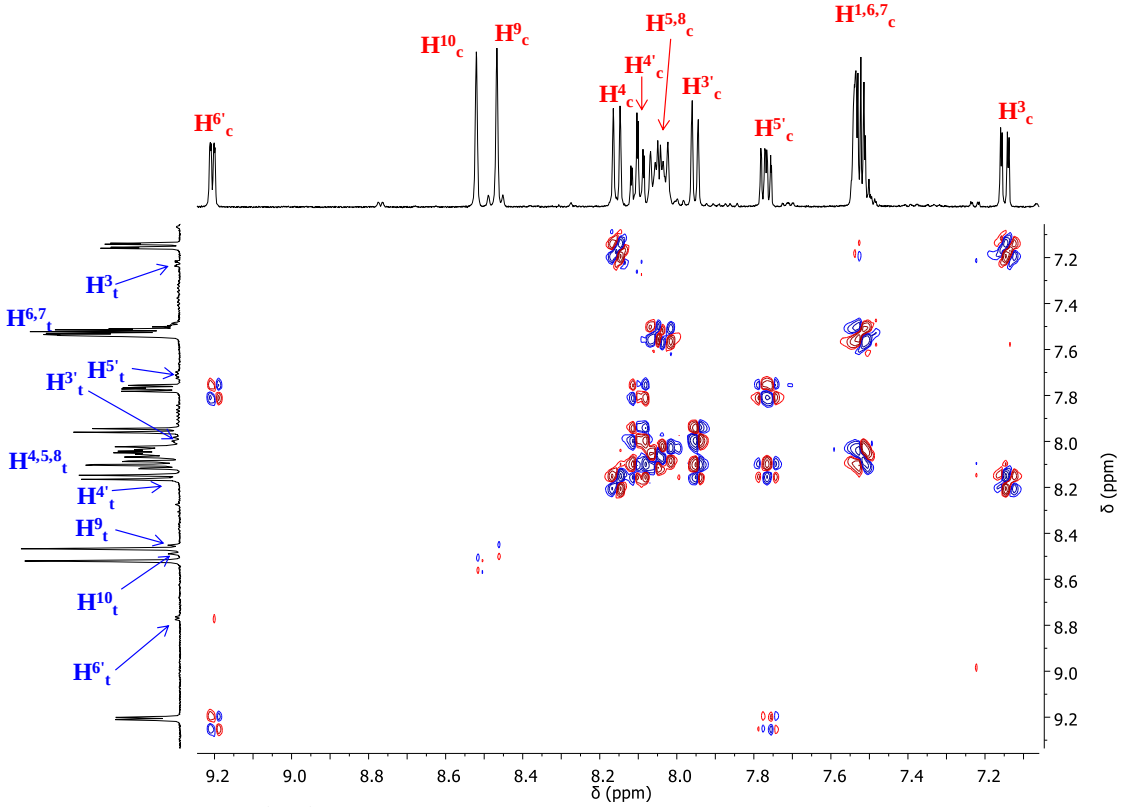

Figure S57. ^{1}H,^{1}H–DQCOSY spectrum (CD_2Cl_2, 298 K) of **8a**, aromatic region.

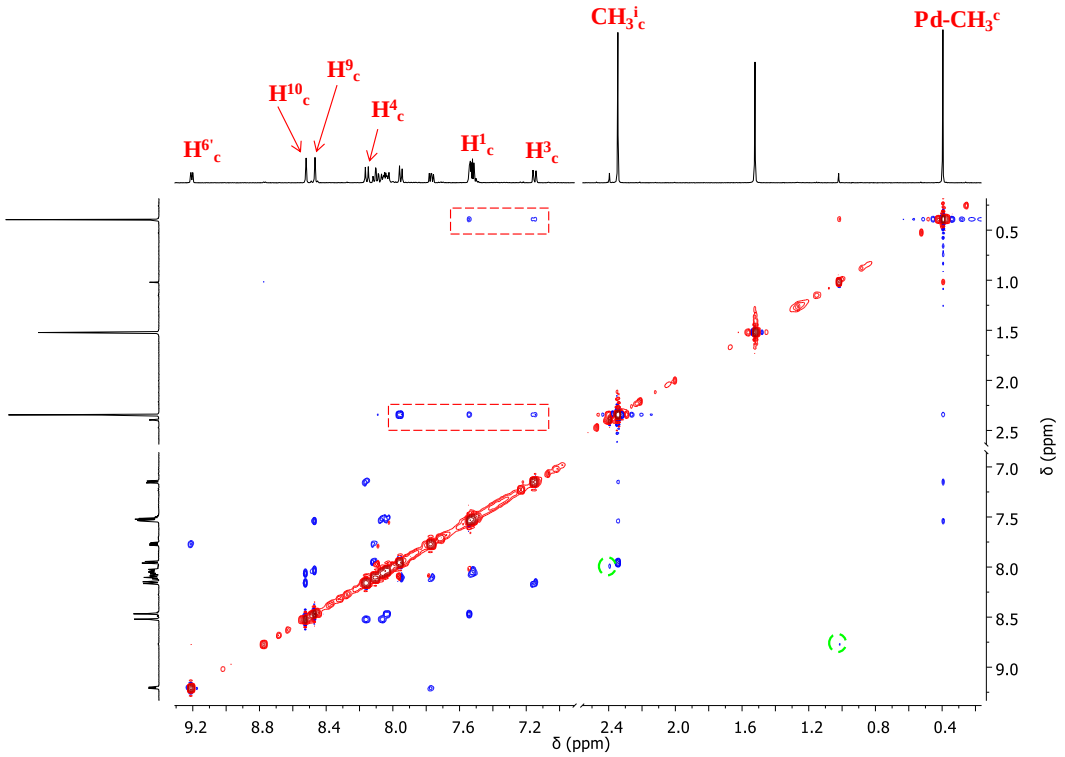

Figure S58. ^{1}H,^{1}H–NOESY spectrum (CD_2Cl_2, 298 K) of **8a** (red = exchange peaks, blue = NOE peaks).

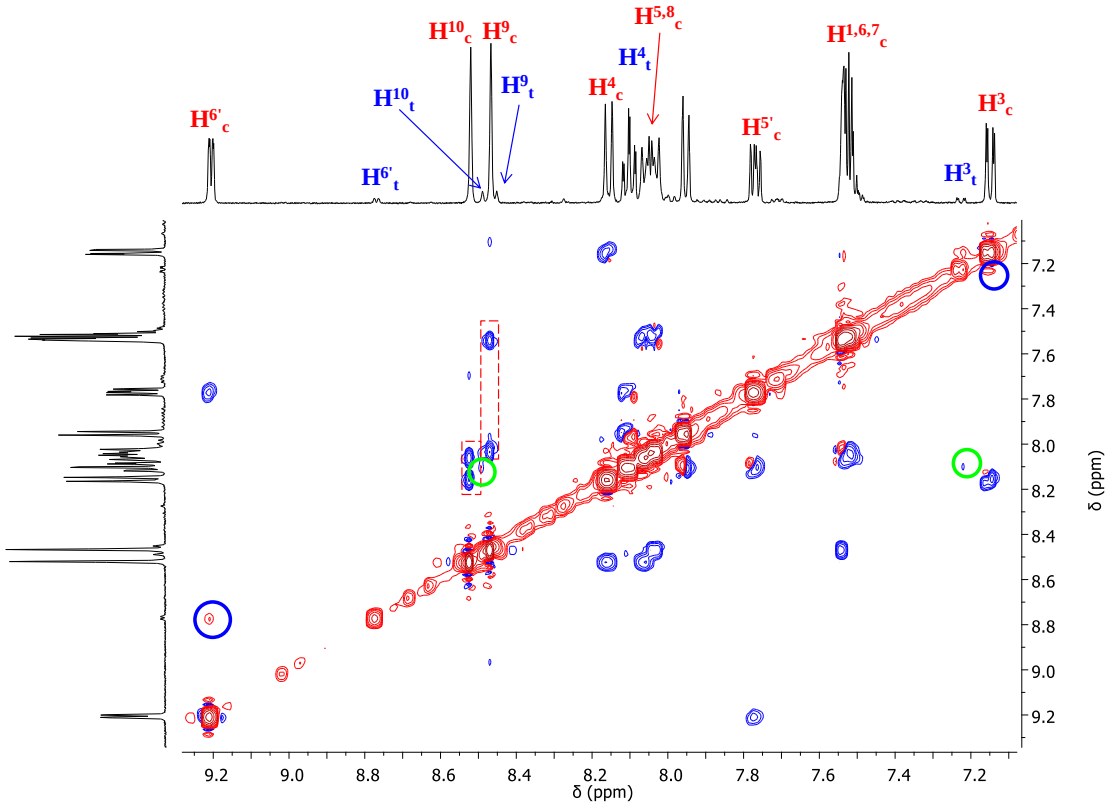

Figure S59. ^{1}H,^{1}H–NOESY spectrum (CD_2Cl_2, 298 K) of **8a**, aromatic region (red = exchange peaks, blue = NOE peaks).

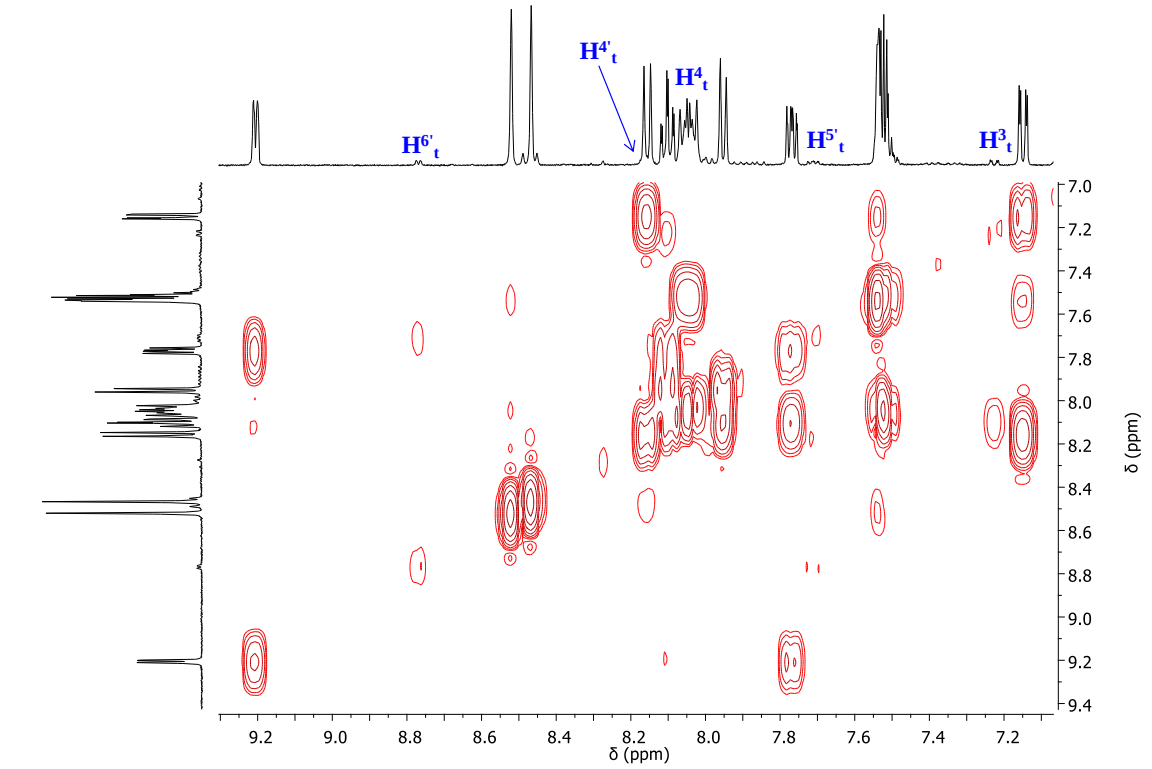

Figure S60. ^{1}H,^{1}H–COSY spectrum (CD_2Cl_2, 298 K) of **8a**, aromatic region.

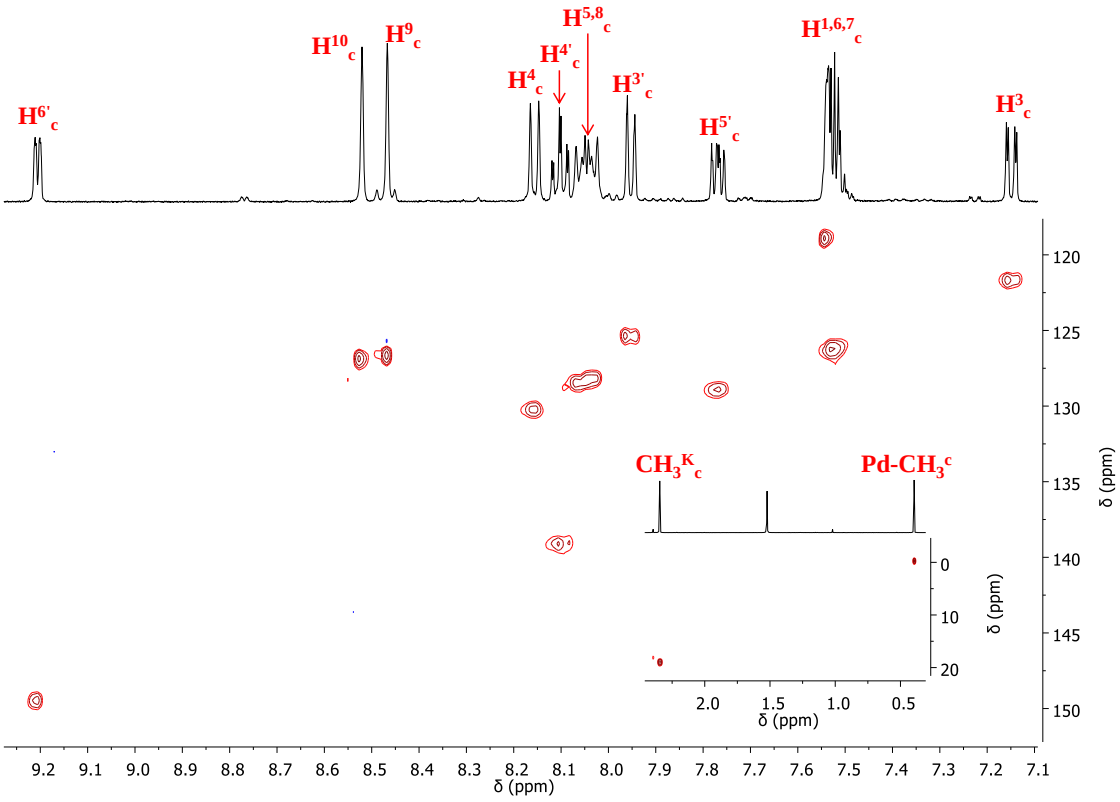

Figure S61. ^{1}H,^{13}C–HSQC spectrum (CD_2Cl_2, 298 K) of **8a** (red = CH/CH_3).

NMR characterization of [Pd(CH$_3$)Cl(9)] 9a (CD$_2$Cl$_2$, T = 298 K)

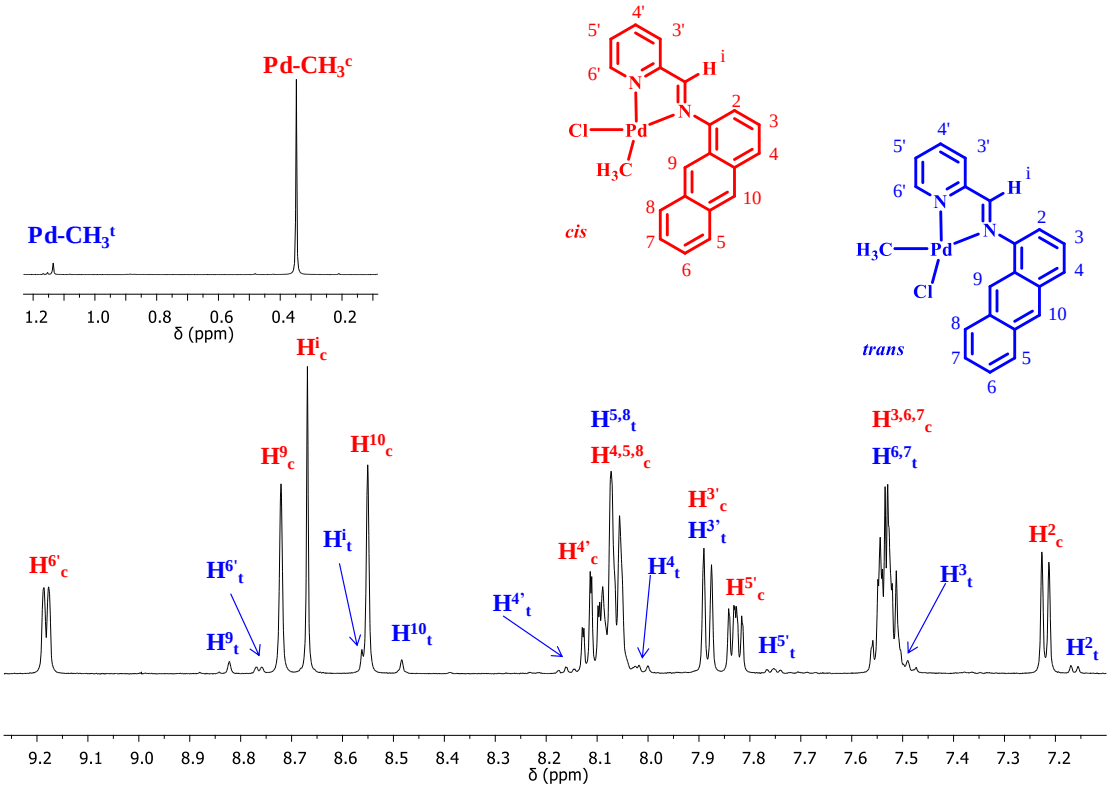

Figure S62. ^{1}H–NMR spectrum (CD$_2$Cl$_2$, 298 K) of **9a**.

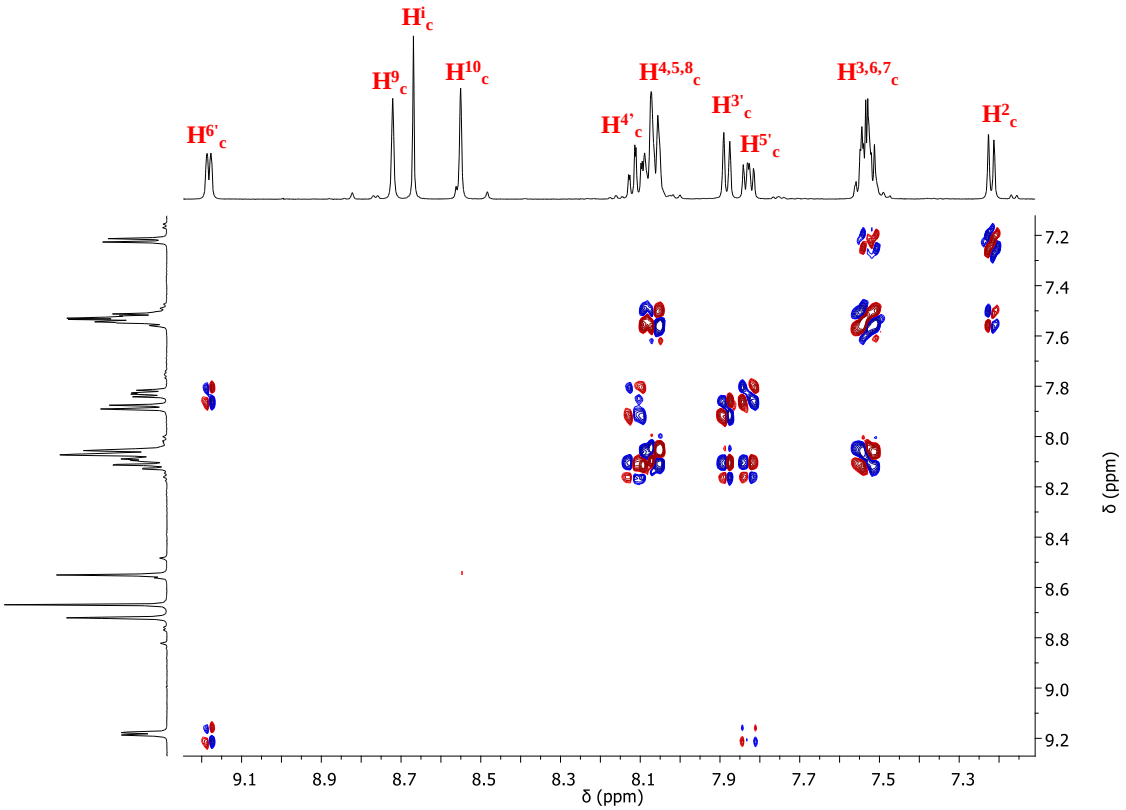

Figure S63. ^{1}H,^{1}H–DQCOSY spectrum (CD$_2$Cl$_2$, 298 K) of **9a**.

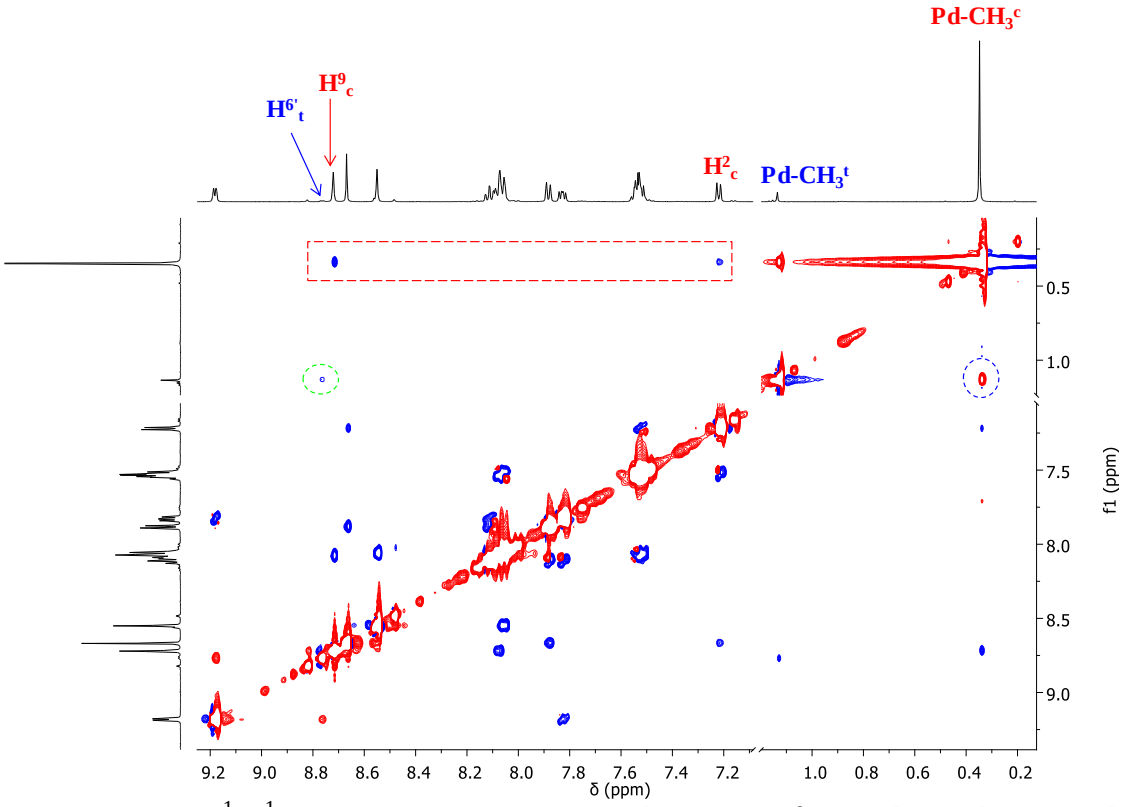

Figure S64. ^{1}H,^{1}H–NOESY spectrum (CD_2Cl_2, 298 K) of **9a** (red = exchange peaks, blue = NOE peaks).

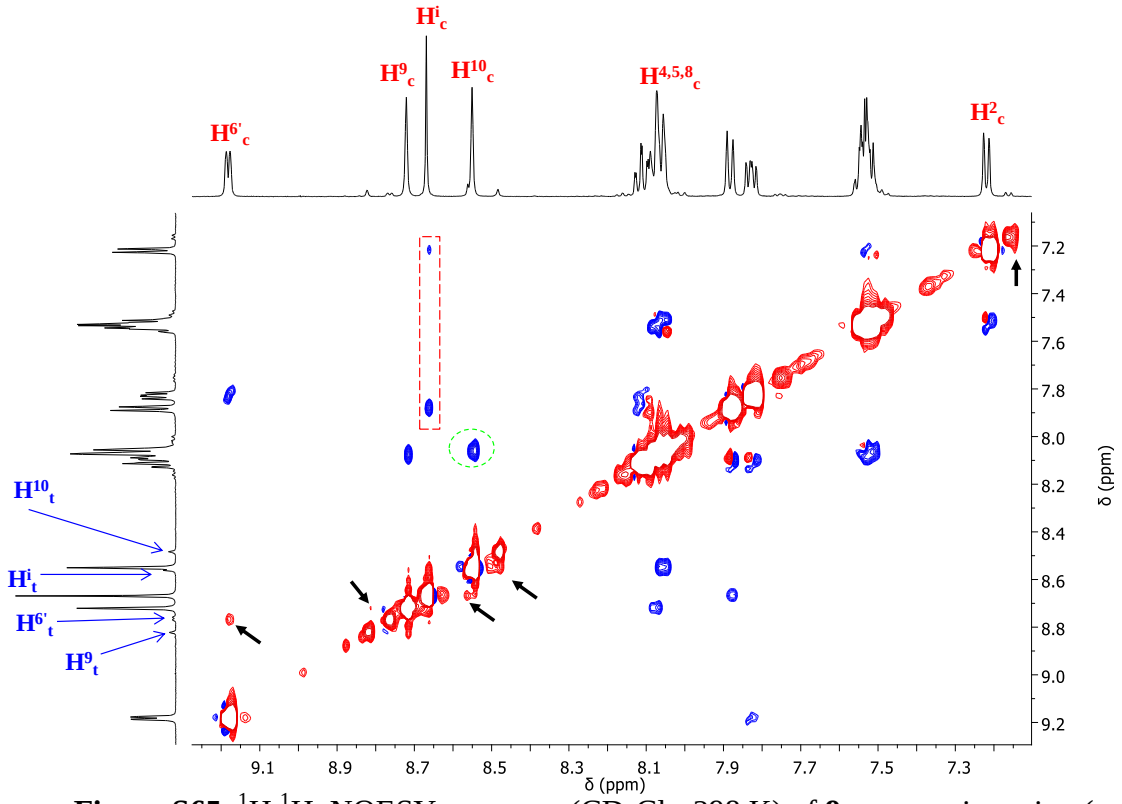

Figure S65. ^{1}H,^{1}H–NOESY spectrum (CD_2Cl_2, 298 K) of **9a**, aromatic region (red: exchange peaks, blue = NOE peaks).

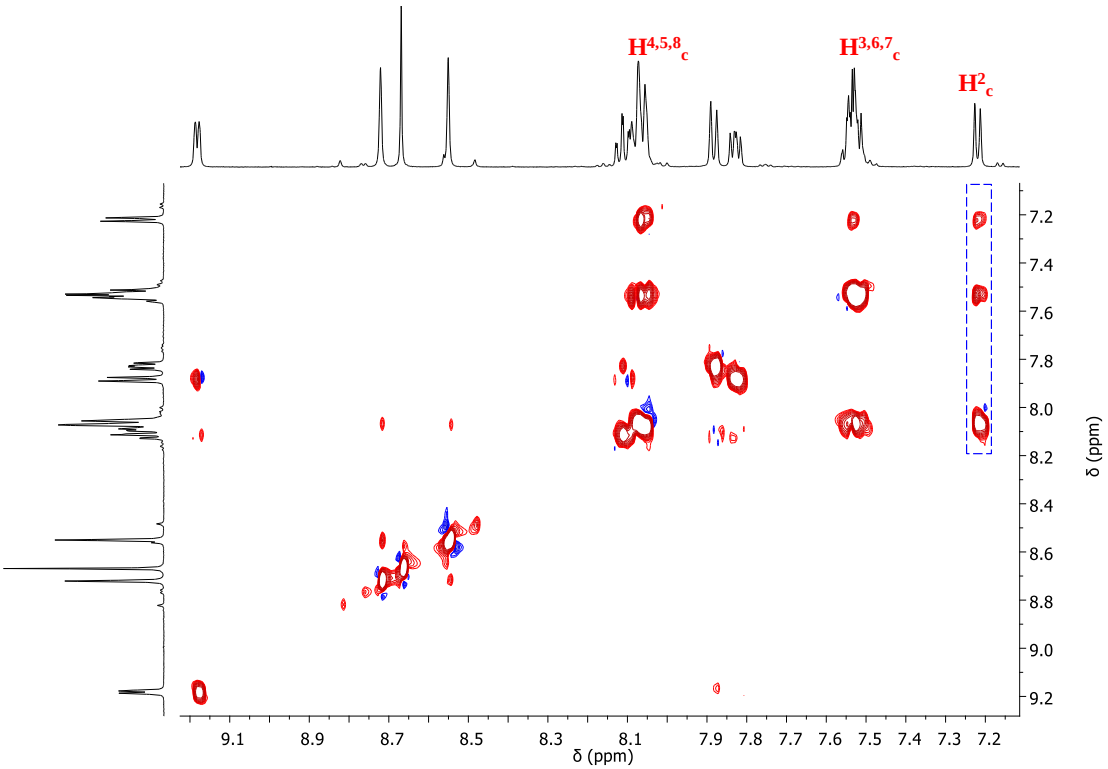

Figure S66. ^{1}H,^{1}H–TOCSY spectrum (CD_2Cl_2, 298 K) of **9a**.

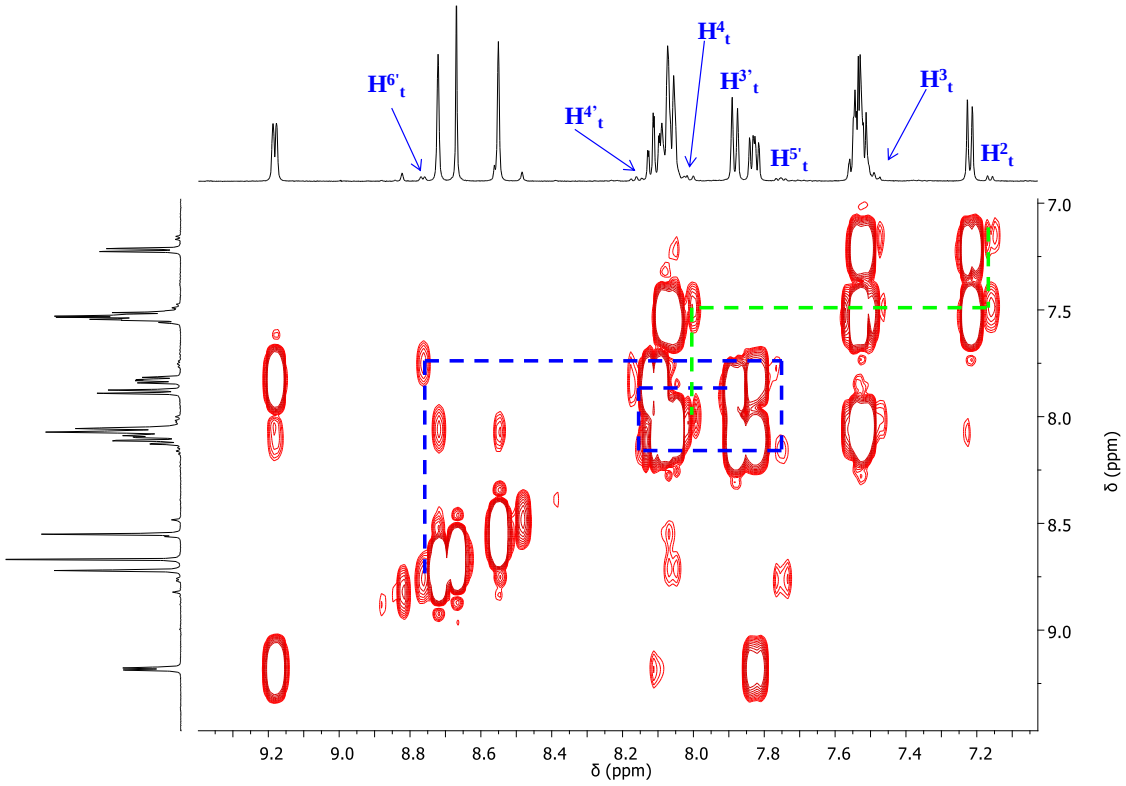

Figure S67. ^{1}H,^{1}H–COSY spectrum (CD_2Cl_2, 298 K) of **9a**.

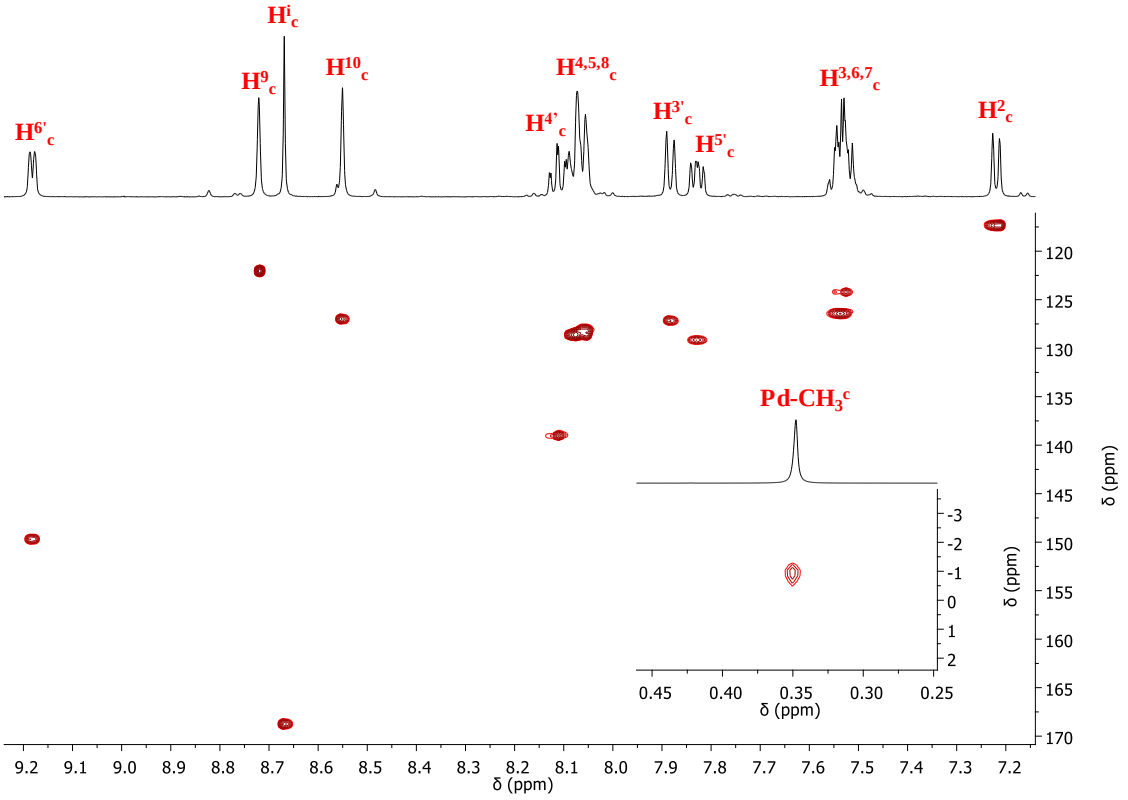

Figure S68. $^{1}H,^{13}C$–HSQC spectrum (CD_2Cl_2, 298 K) of **9a**.

NMR characterization of [Pd(CH$_3$)(NCCH$_3$)(1)][PF$_6$] 1b (CD$_2$Cl$_2$, T = 298 K)

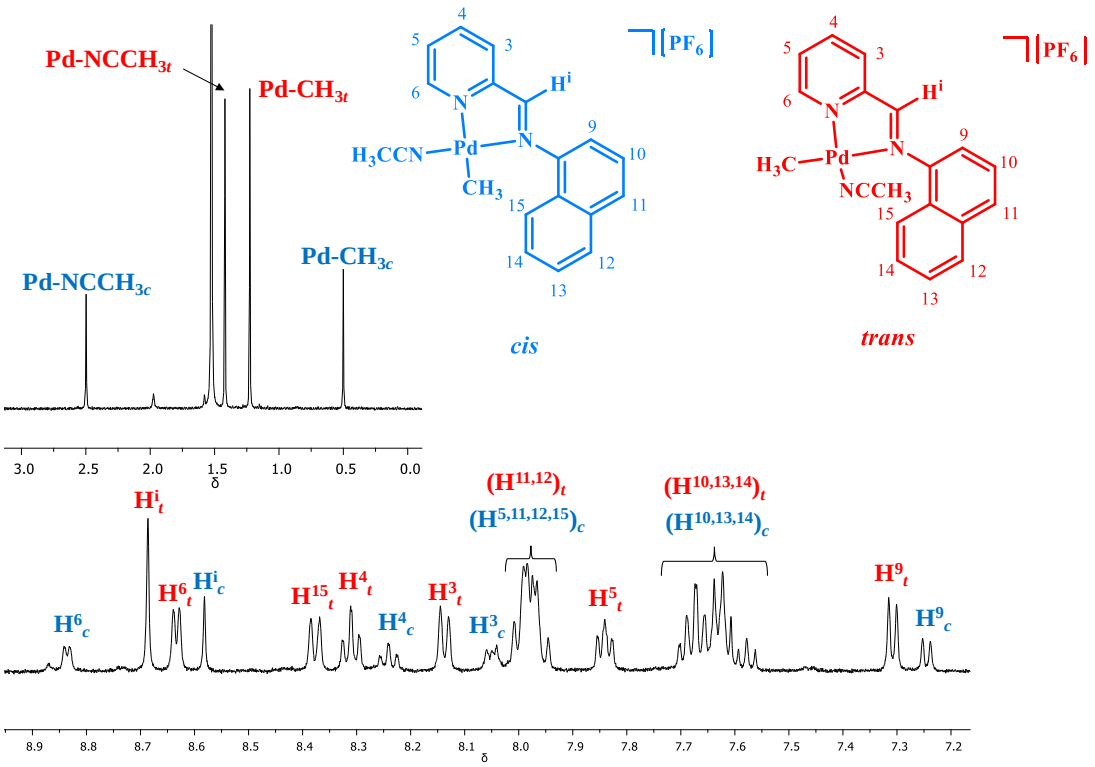

Figure S69. ^{1}H NMR spectrum (CD_2Cl_2, T= 298 K) of **1b** (aromatic and aliphatic region not on scale).

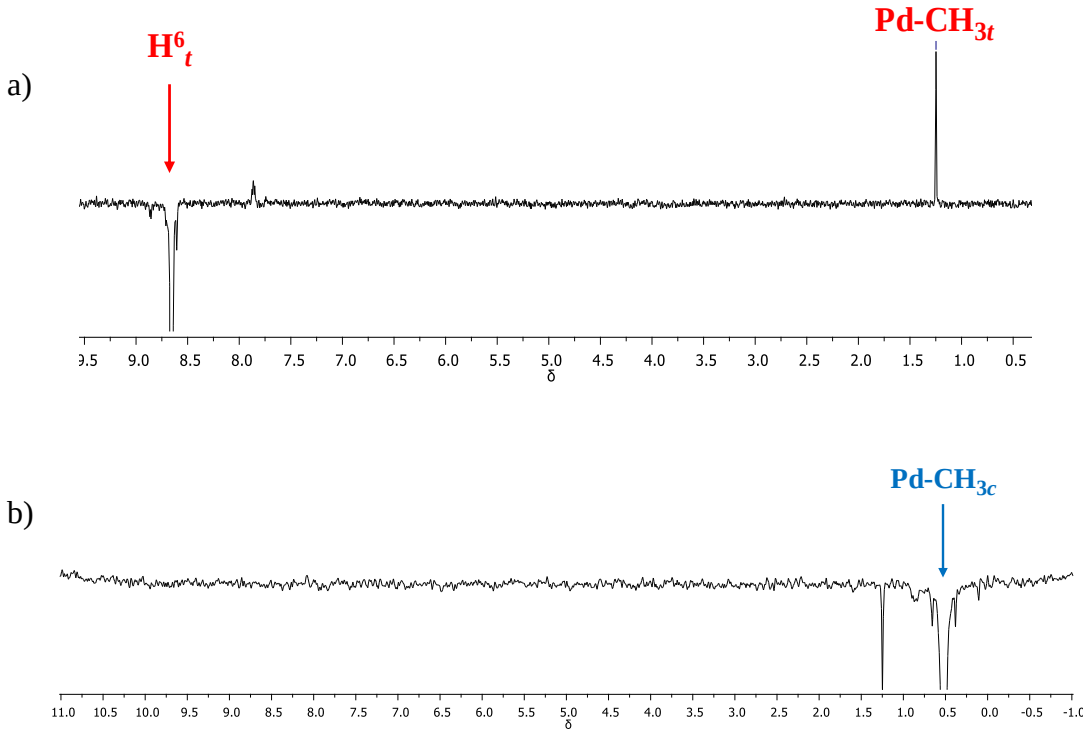

Figure S70. NOESY1D spectra (CD_2Cl_2, T= 298 K) of **1b**: a) irradiated signal at 8.63 ppm; b) irradiated signal at 0.50 ppm.

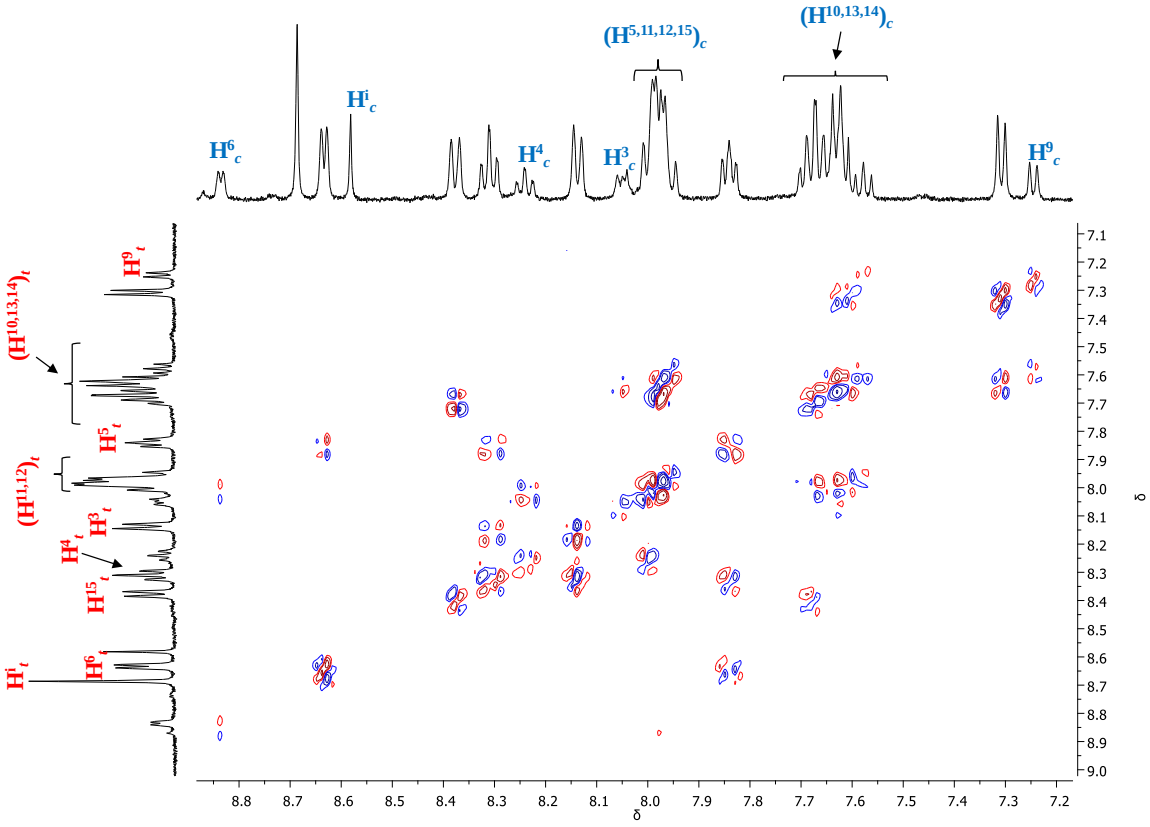

Figure S71. $^1H,^1H$-DQCOSY spectrum (CD_2Cl_2, T= 298 K) of **1b**.

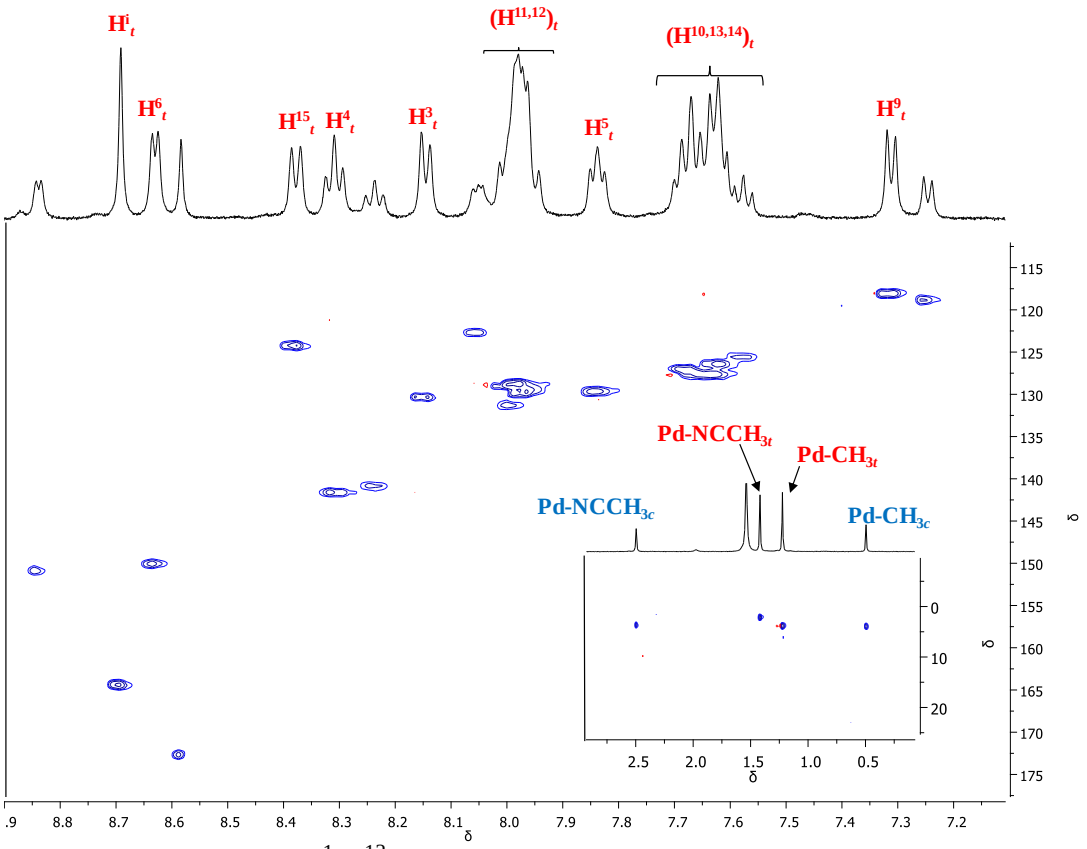

Figure S72. ^{1}H,^{13}C-HSQC spectrum (CD_2Cl_2, T= 298 K) of **1b**.

NMR characterization of [Pd(CH$_3$)(NCCH$_3$)(2)][PF$_6$] 2b (CD_2Cl_2, T = 298 K)

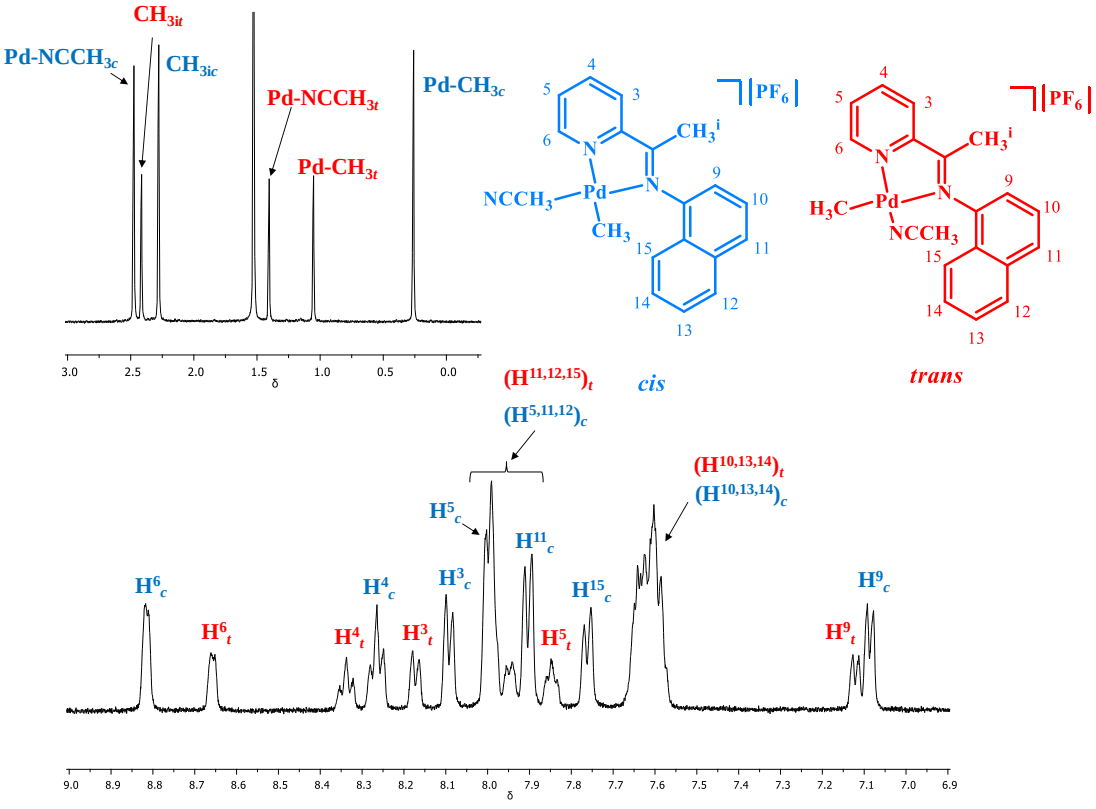

Figure S73. ^{1}H NMR spectrum (CD_2Cl_2, T= 298 K) of **2b**.

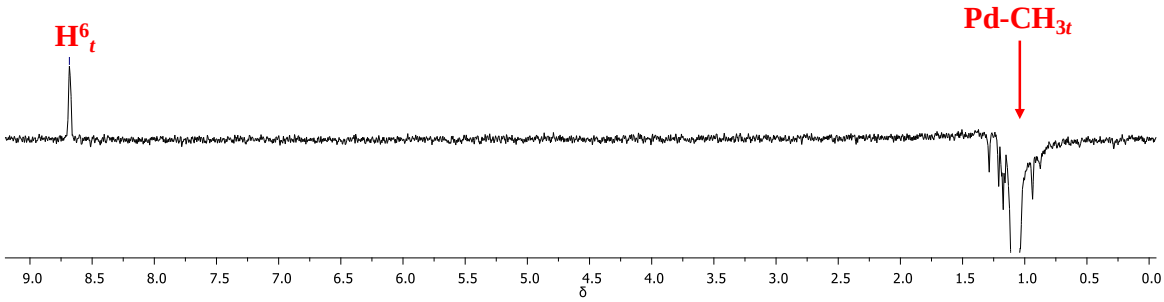

Figure S74. NOESY1D spectrum (CD_2Cl_2, T= 298 K) of **2b**: irradiated signal at 1.05 ppm.

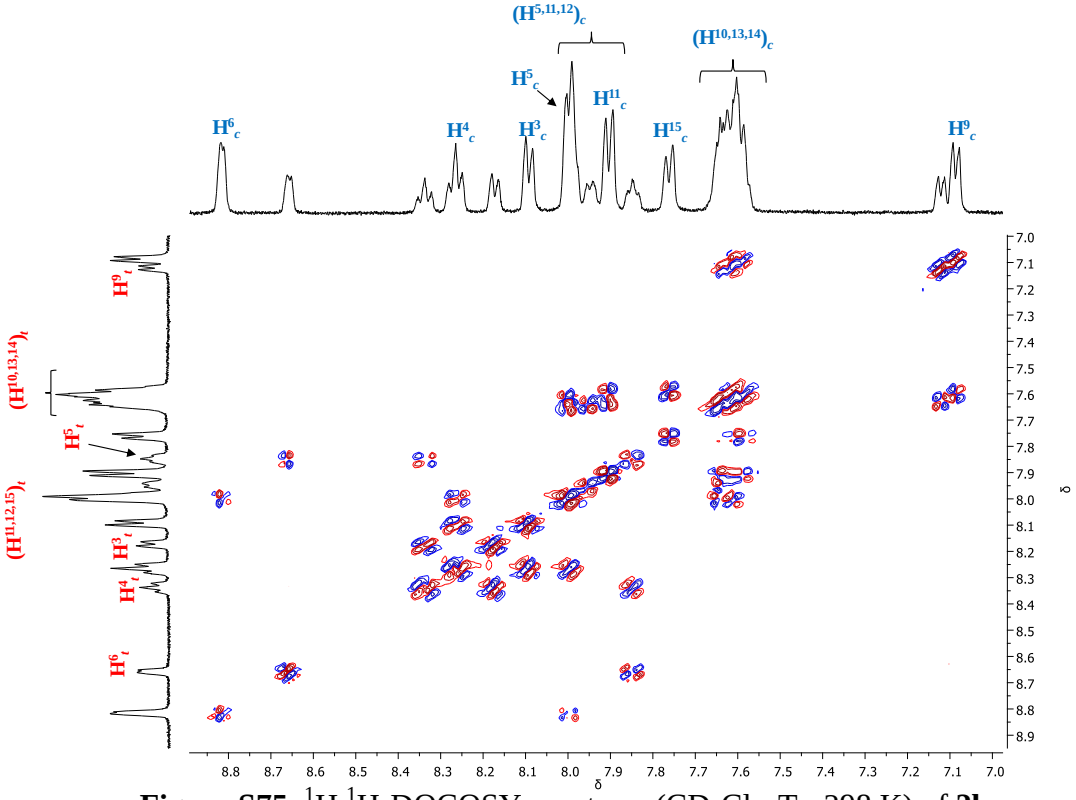

Figure S75. $^1H,^1H$-DQCOSY spectrum (CD_2Cl_2, T= 298 K) of **2b**.

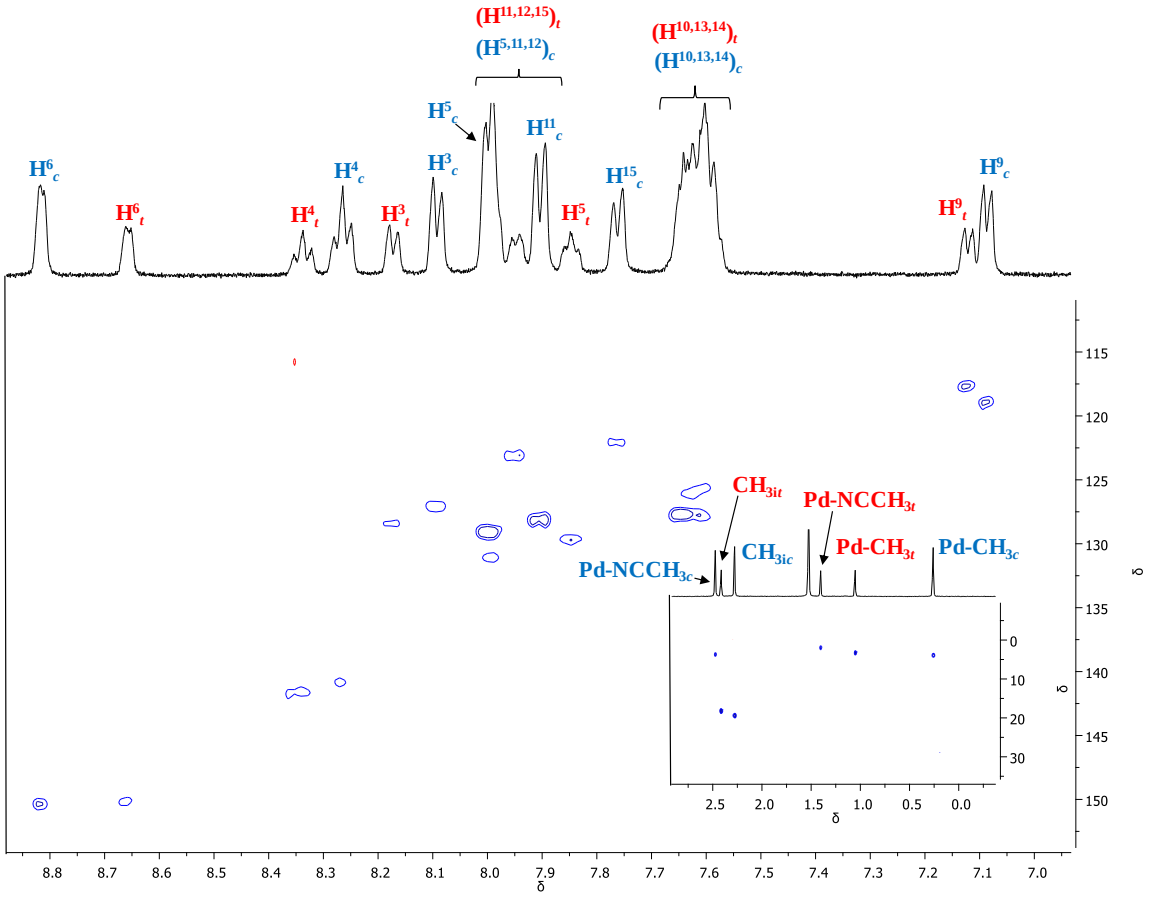

Figure S76. $^{1}H,^{13}C$-HSQC spectrum (CD_2Cl_2, T= 298 K) of **2b** (blue = CH/CH_3).

NMR characterization of [Pd(CH$_3$)(NCCH$_3$)(3)][PF$_6$] 3b (CD$_2$Cl$_2$, T = 253 K)

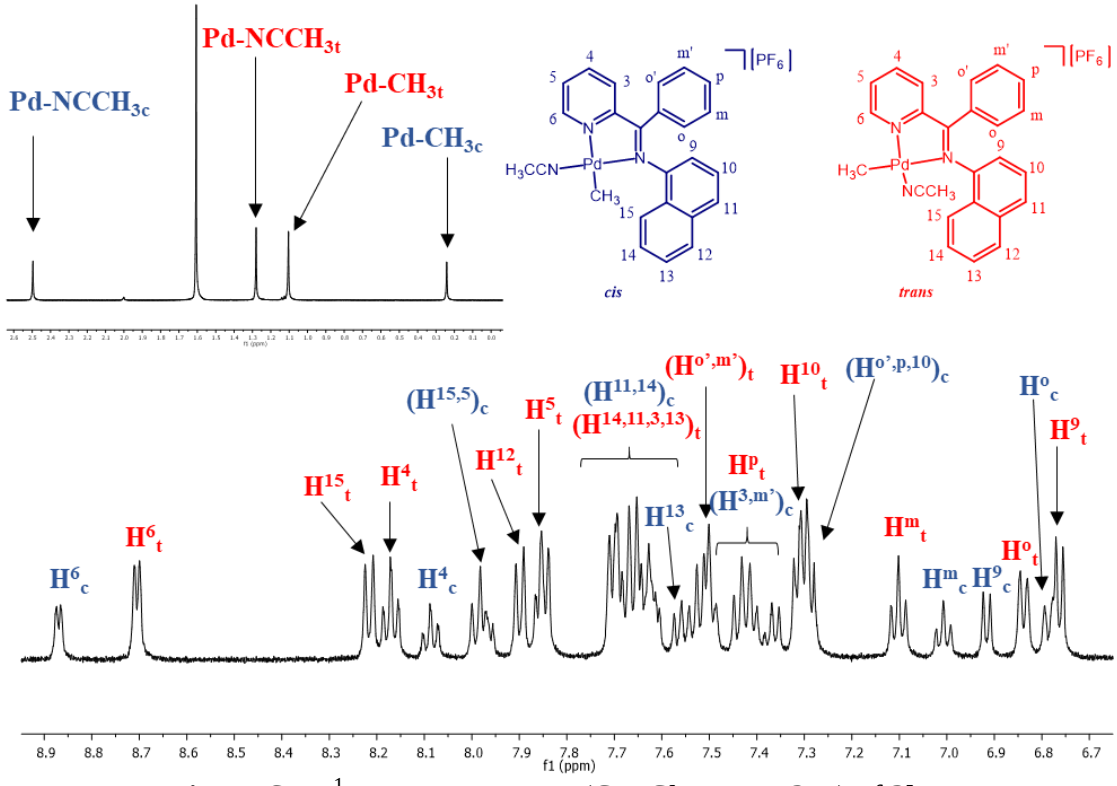

Figure S77. ^{1}H NMR spectrum (CD_2Cl_2, T = 253 K) of **3b**.

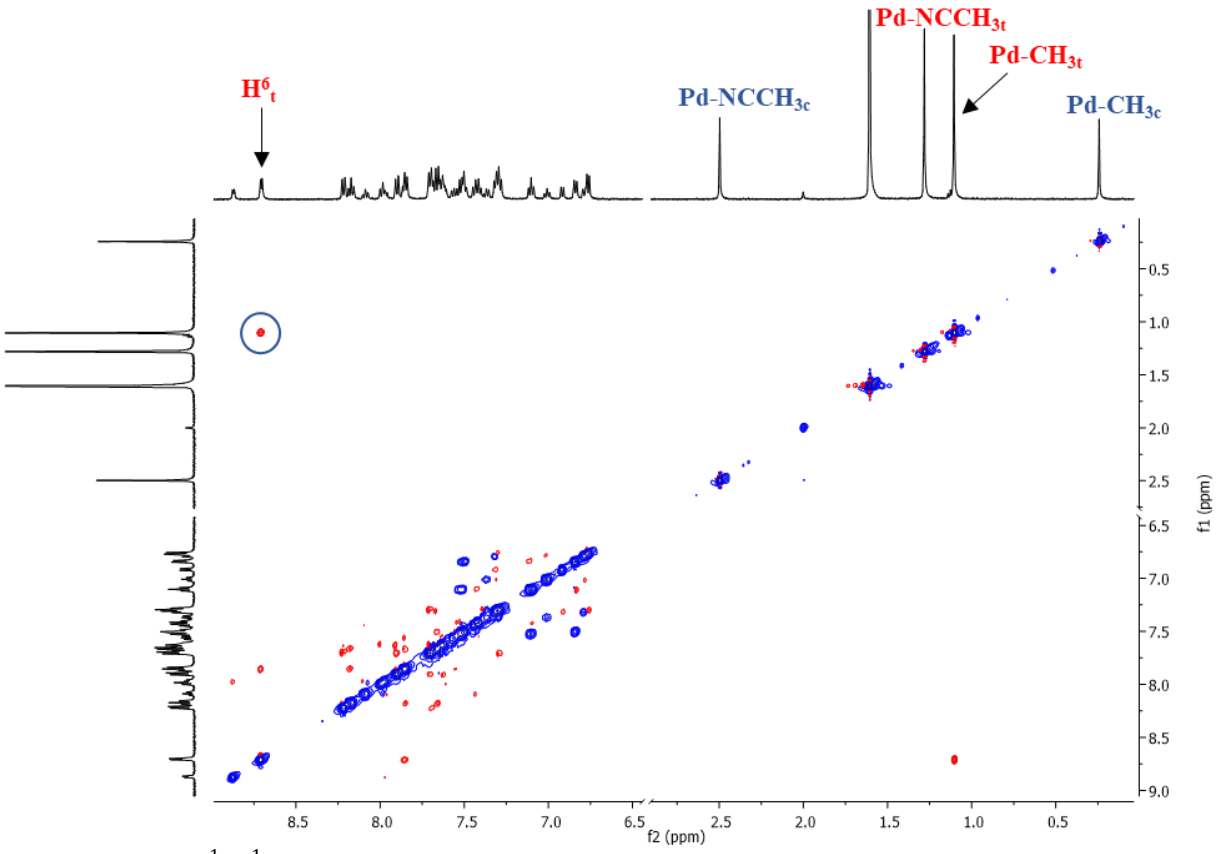

Figure S78. $^{1}H,^{1}H$-NOESY spectrum (CD_2Cl_2, T = 253 K) of **3b** (blue = NOE between Pd-CH_{3trans} and H^{6}_{trans}).

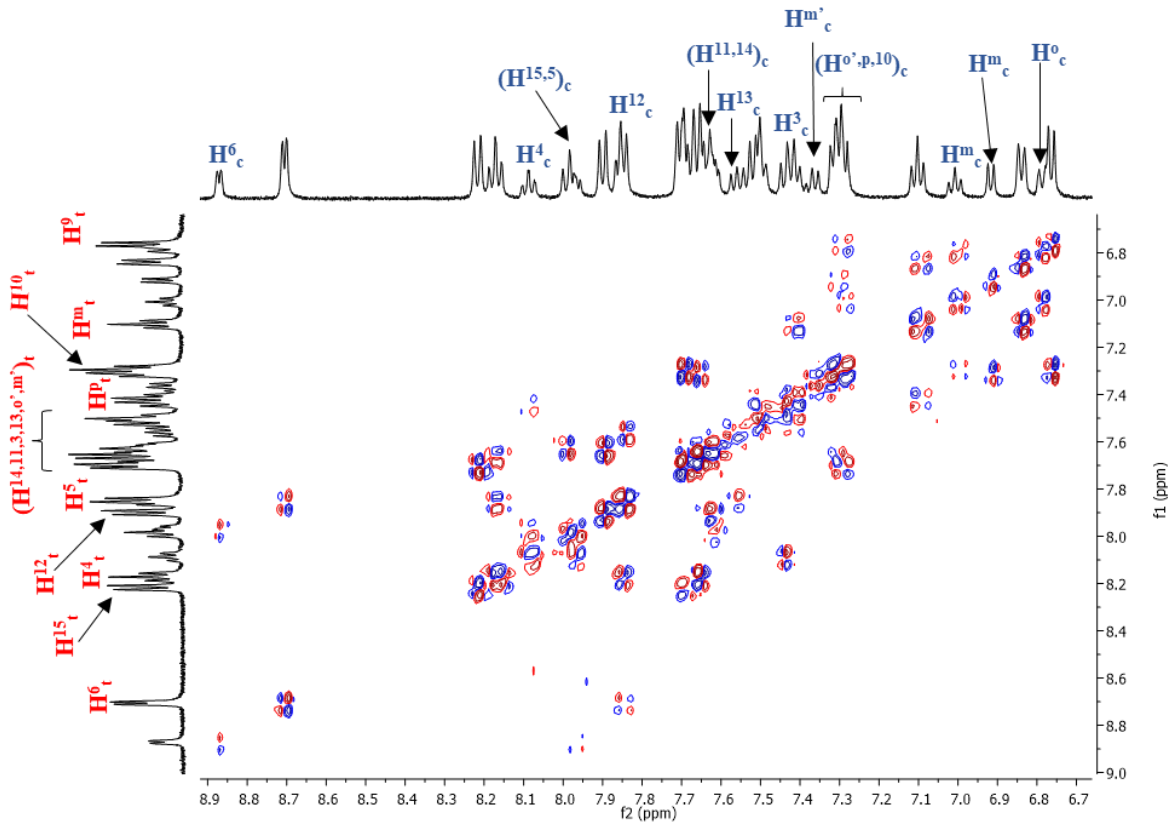

Figure S79. ^{1}H-^{1}H DQCOSY spectrum (CD_2Cl_2, T = 253 K) of **3b**.

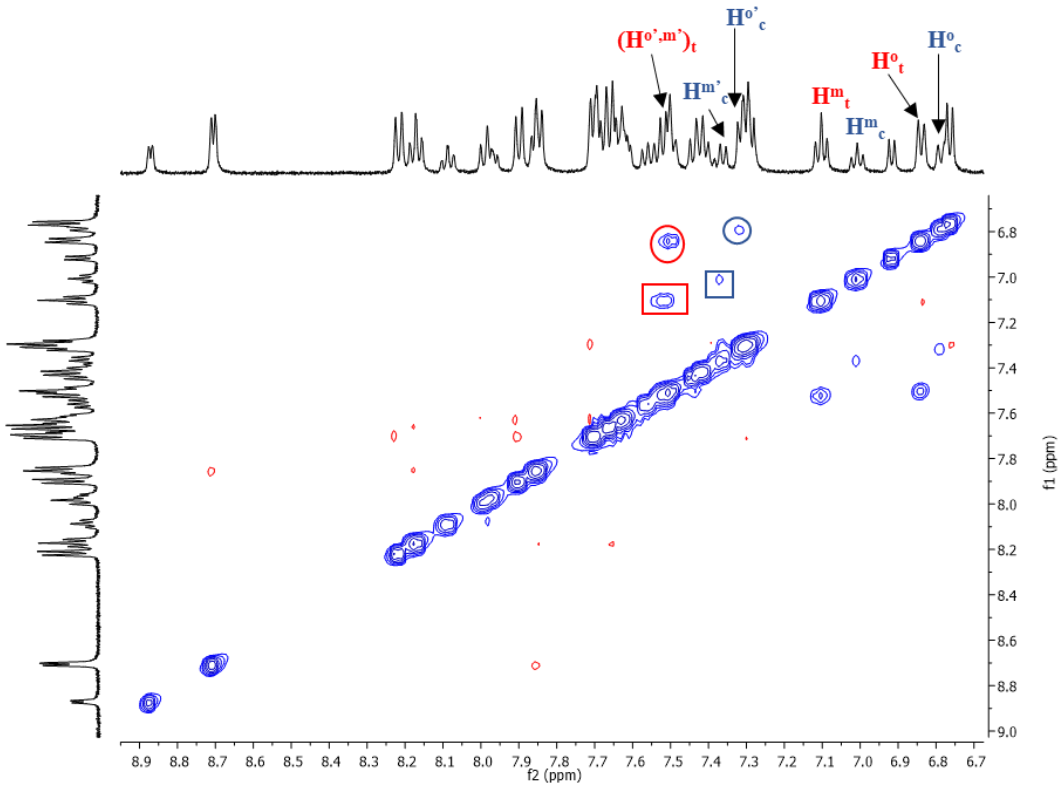

Figure S80. ^{1}H,^{1}H-NOESY spectrum (CD_2Cl_2, T = 253 K) of **3b**, aromatic region (blue = exchange peaks, red = NOE peaks).

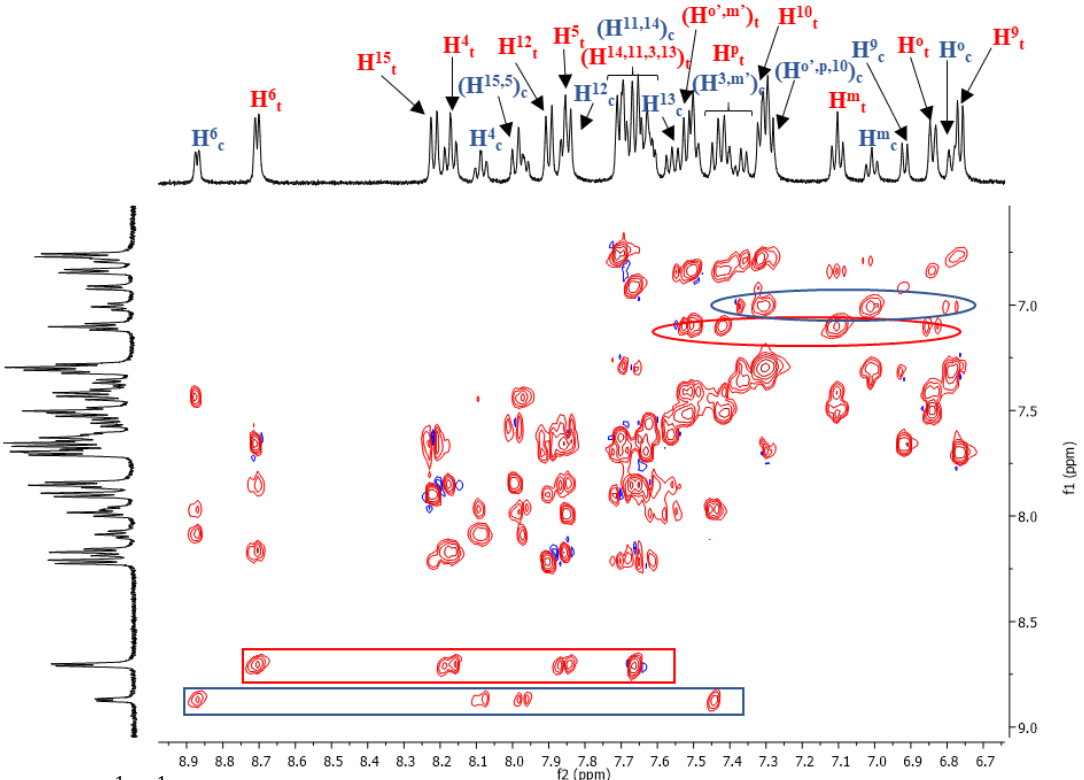

Figure S81. ^{1}H,^{1}H-TOCSY spectrum (CD_2Cl_2, T = 253 K) of complex **3b**. (blue circle = phenyl group, *cis* species; red circle = phenyl group, *trans* species; blue rectangle = pyridine, *cis*; red rectangle = pyridine, *trans*).

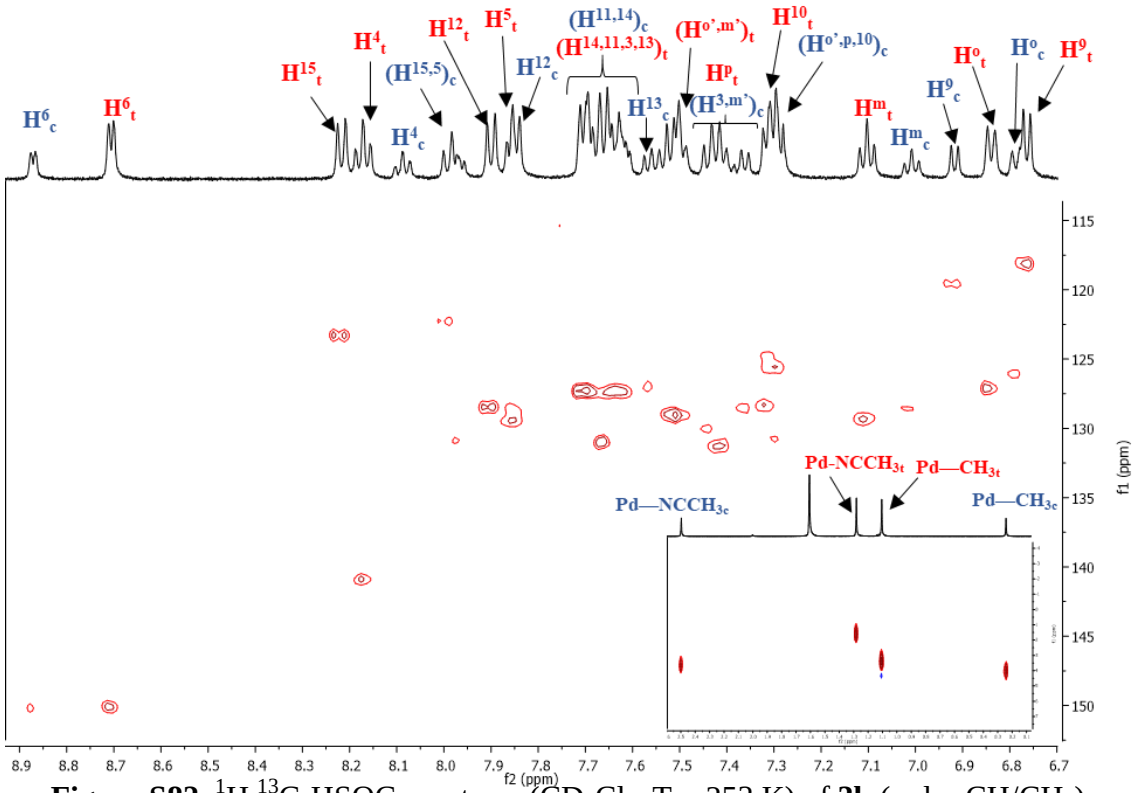

Figure S82. $^{1}H,^{13}C$-HSQC spectrum (CD_2Cl_2, T = 253 K) of **3b** (red = CH/CH_3).

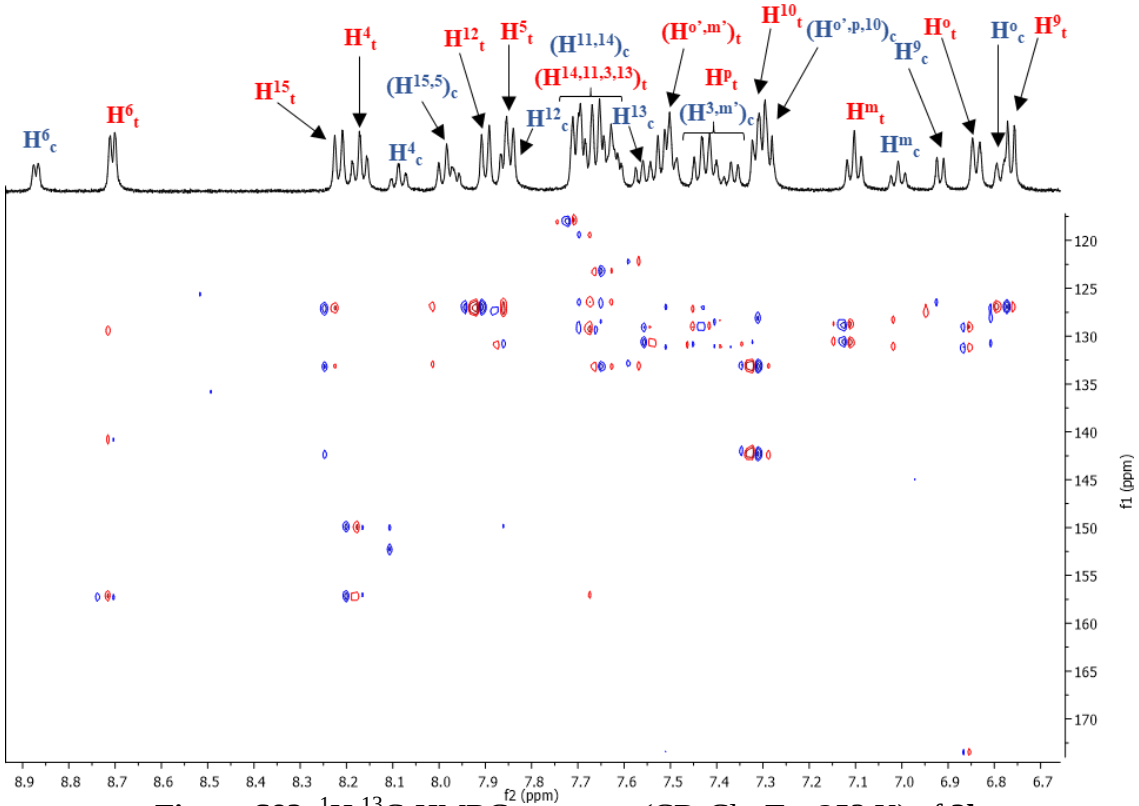

Figure S83. $^{1}H,^{13}C$-HMBC spectrum (CD_2Cl_2, T = 253 K) of **3b**.

NMR characterization of [Pd(CH_3)($NCCH_3$)(4)][PF_6] 4b (CD_2Cl_2, T = 298 K)

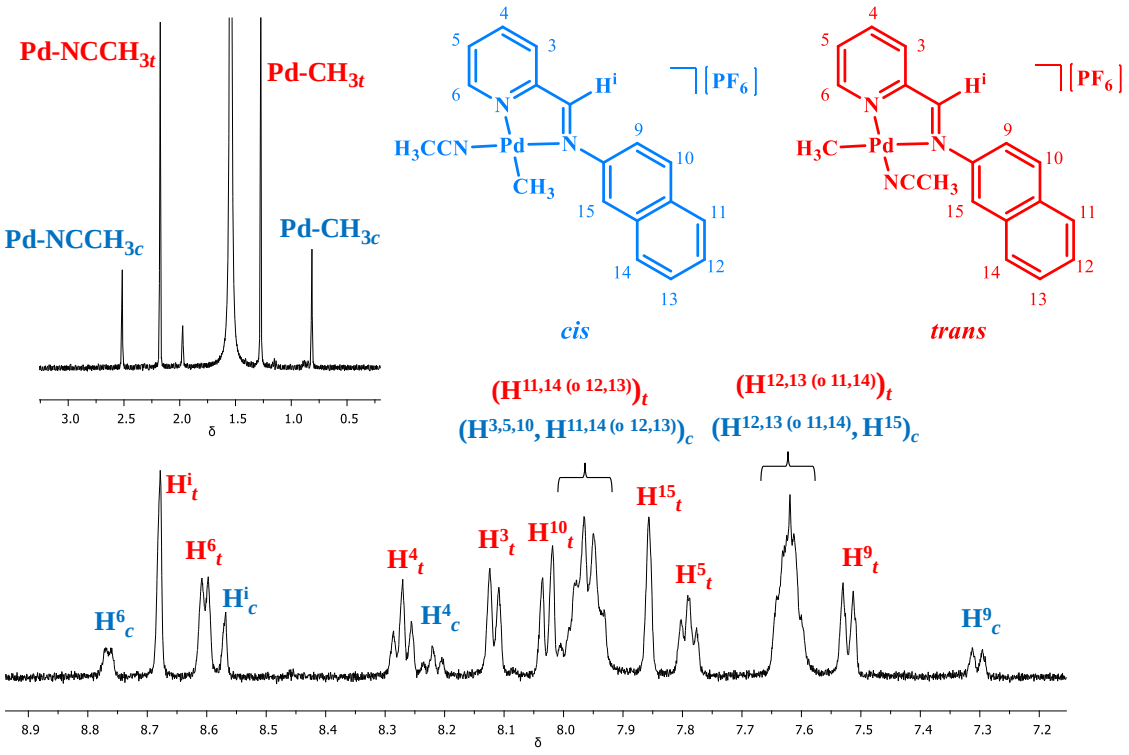

Figure S84. ^{1}H NMR spectrum (CD_2Cl_2, T= 298 K) of **4b**.

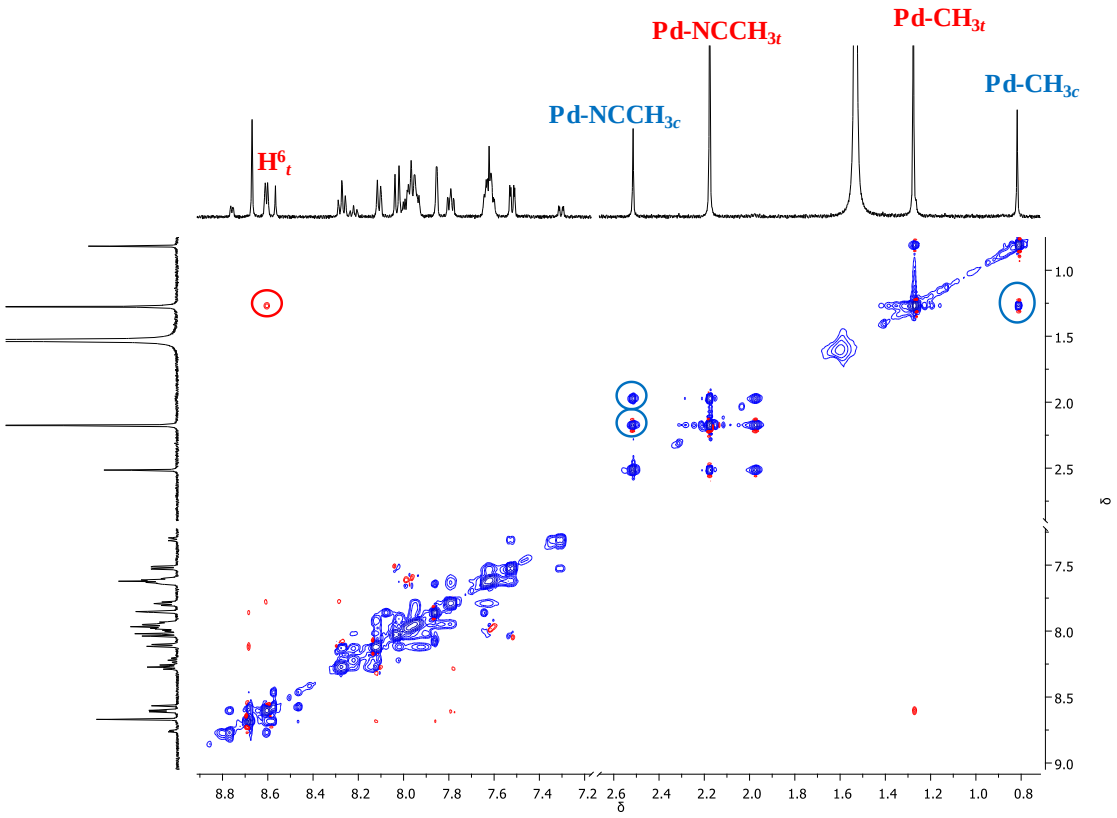

Figure S85. NOESY spectrum (CD_2Cl_2, T= 298 K) of **4b** (blue = exchange peaks, red = NOE peaks).

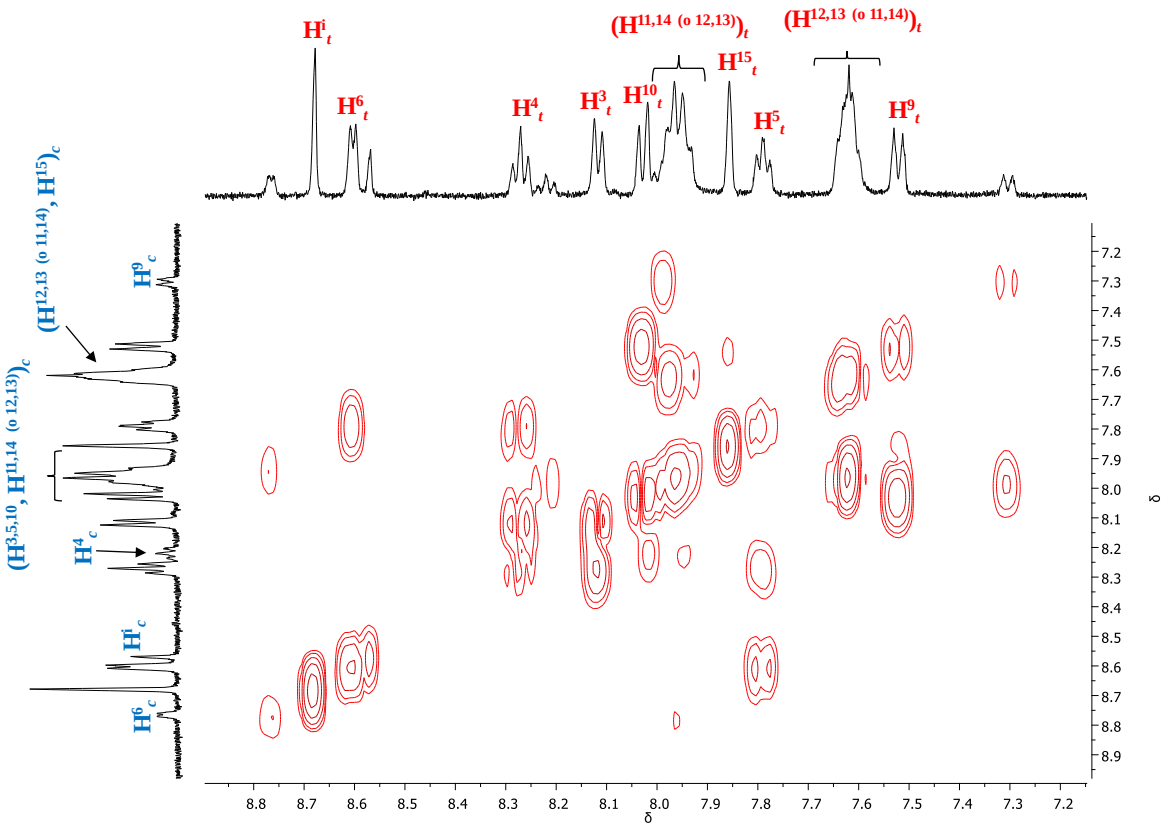

Figure S86. ^{1}H,^{1}H-COSY spectrum (CD_2Cl_2, T= 298 K) of **4b**.

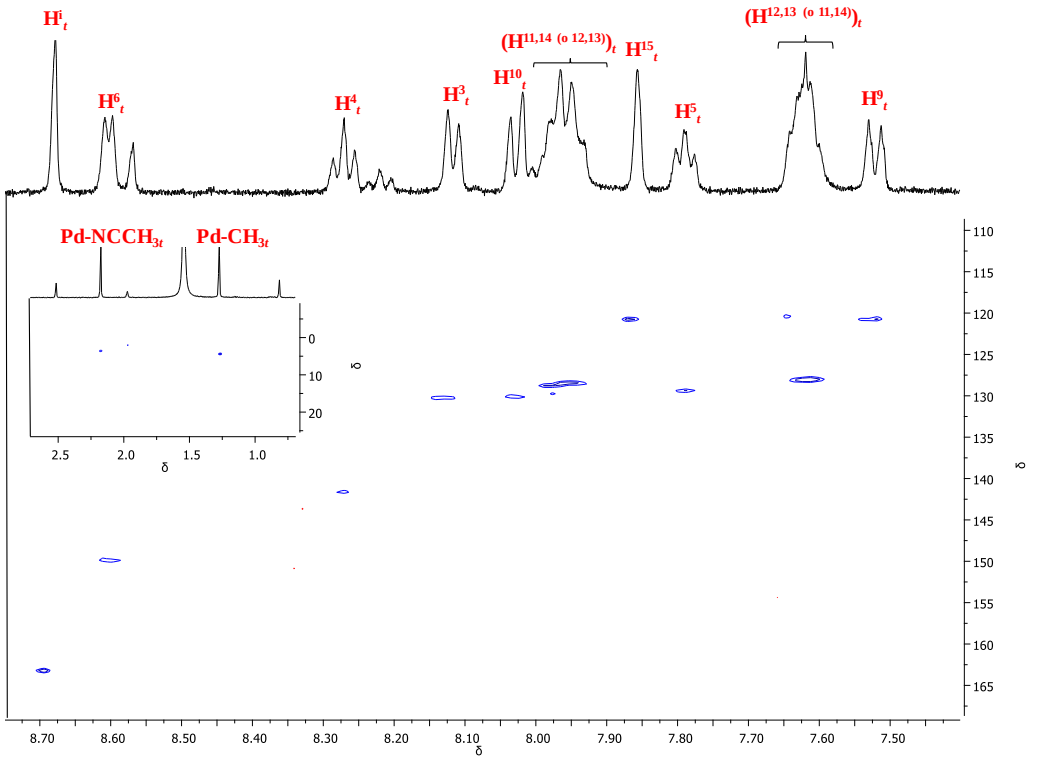

Figure S87. ^{1}H,^{13}C-HSQC spectrum (CD_2Cl_2, T= 298 K) of **4b** (blue = CH/CH_3).

NMR characterization of [Pd(CH_3)($NCCH_3$)(5)][PF_6] 5b (CD_2Cl_2, T = 298 K)

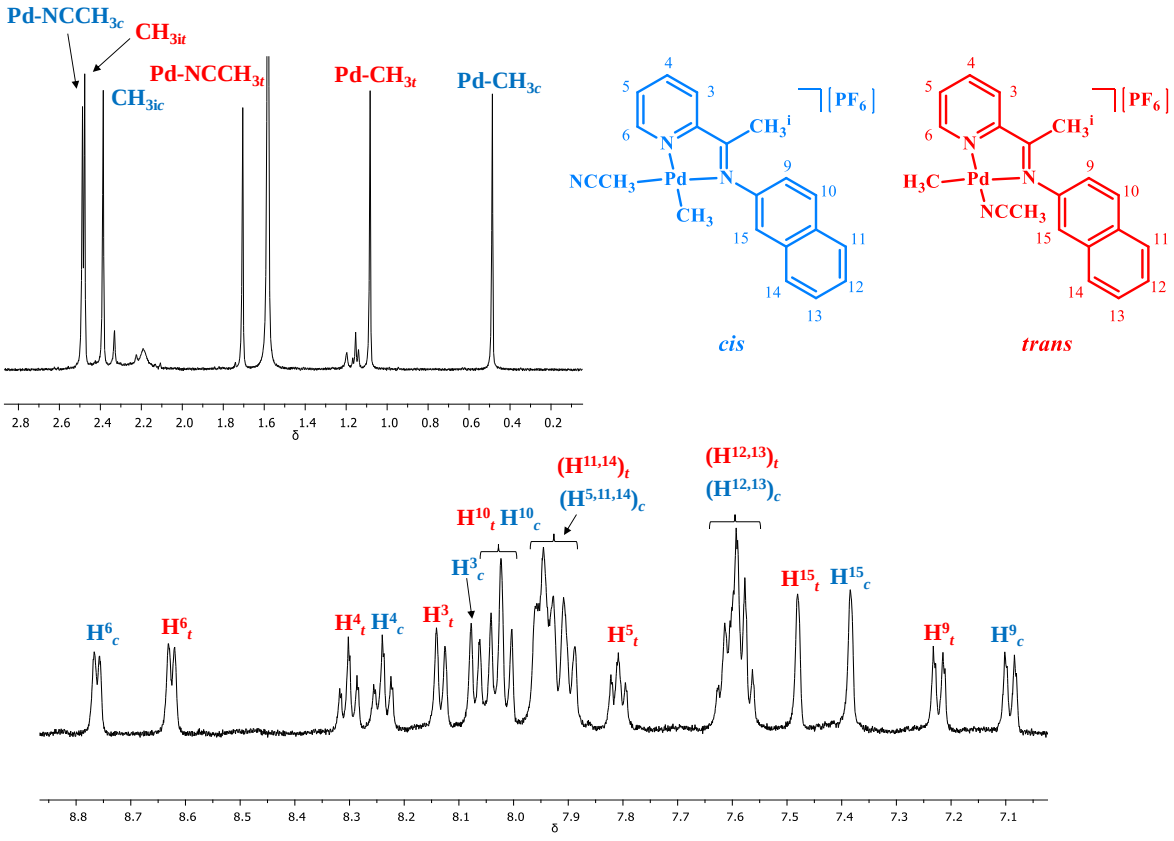

Figure S88. ^{1}H NMR spectrum (CD_2Cl_2, T= 298 K) of **5b**.

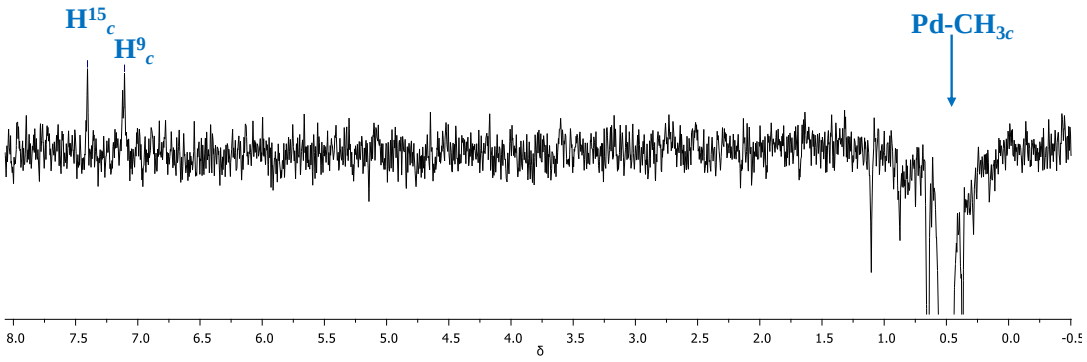

Figure S89. NOESY1D spectrum (CD_2Cl_2, T= 298K) of **5b**: irradiated signal at 0.49 ppm.

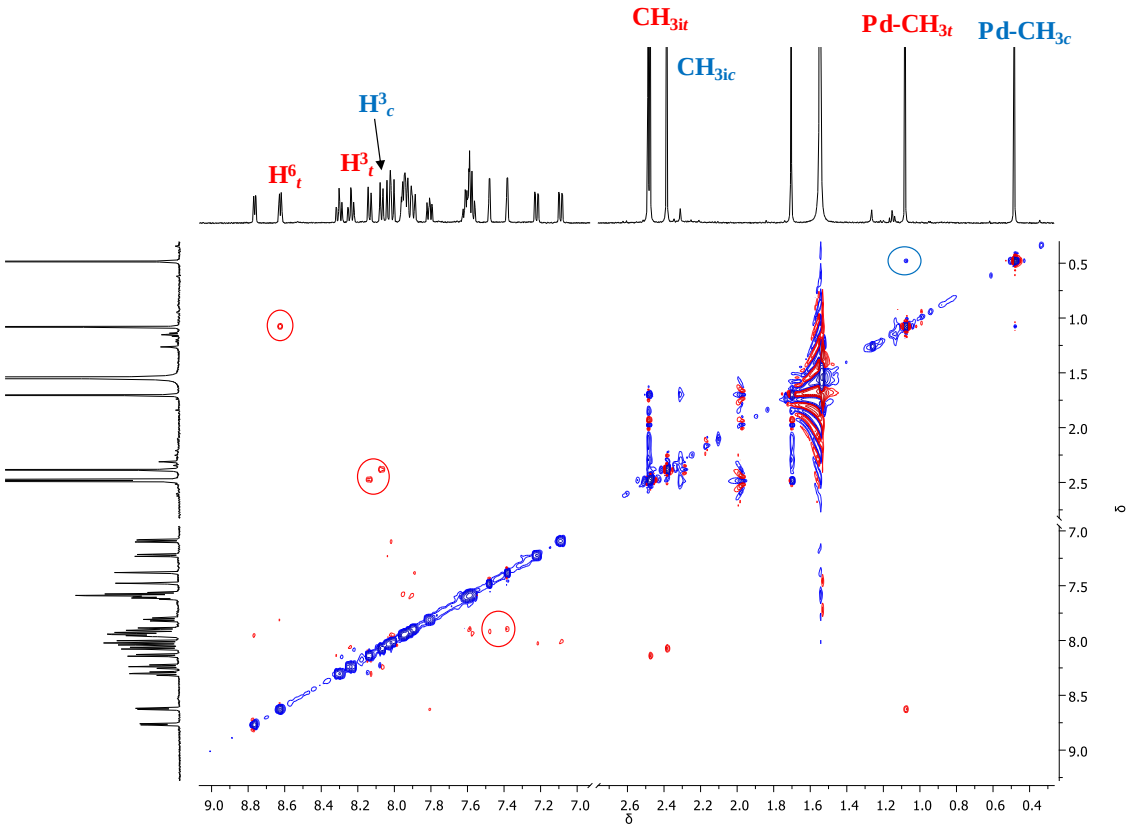

Figure S90. ^{1}H,^{1}H-NOESY spectrum (CD_2Cl_2, T= 298K) of **5b** (blue = exchange peaks, red = NOE peaks).

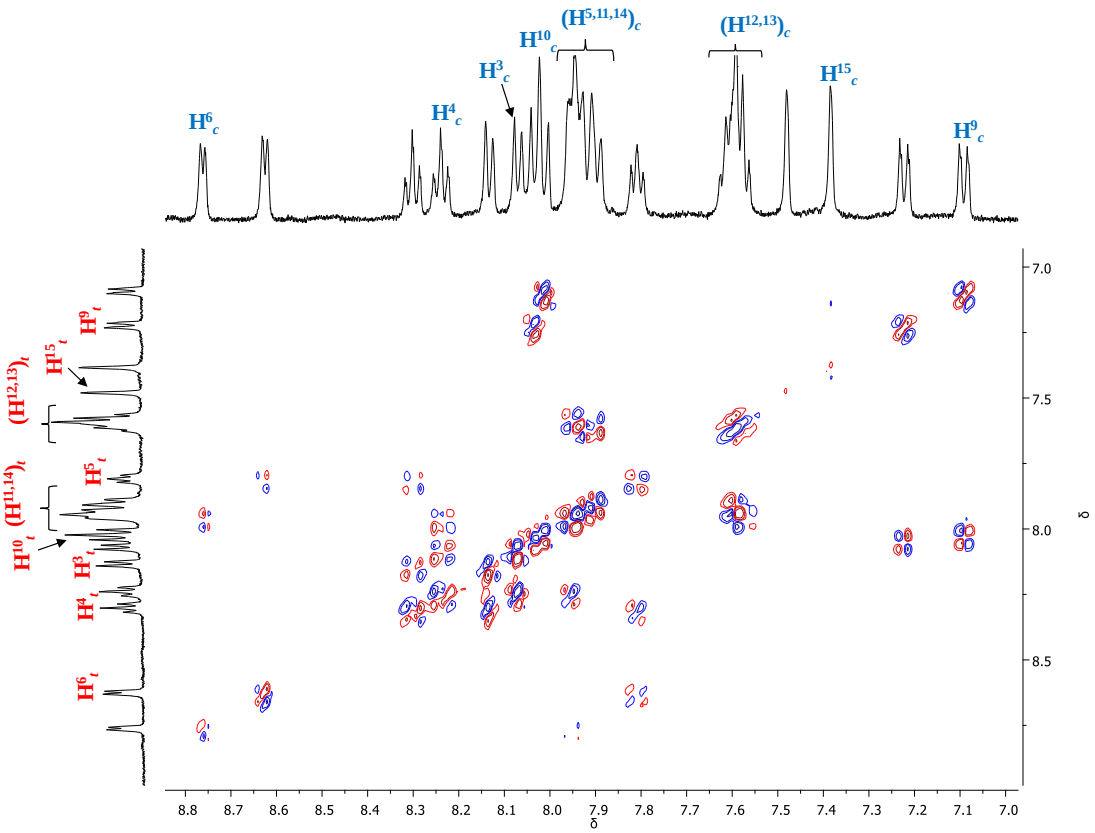

Figure S91. ^{1}H,^{1}H-DQCOSY spectrum (CD_2Cl_2, T= 298 K) of **5b**.

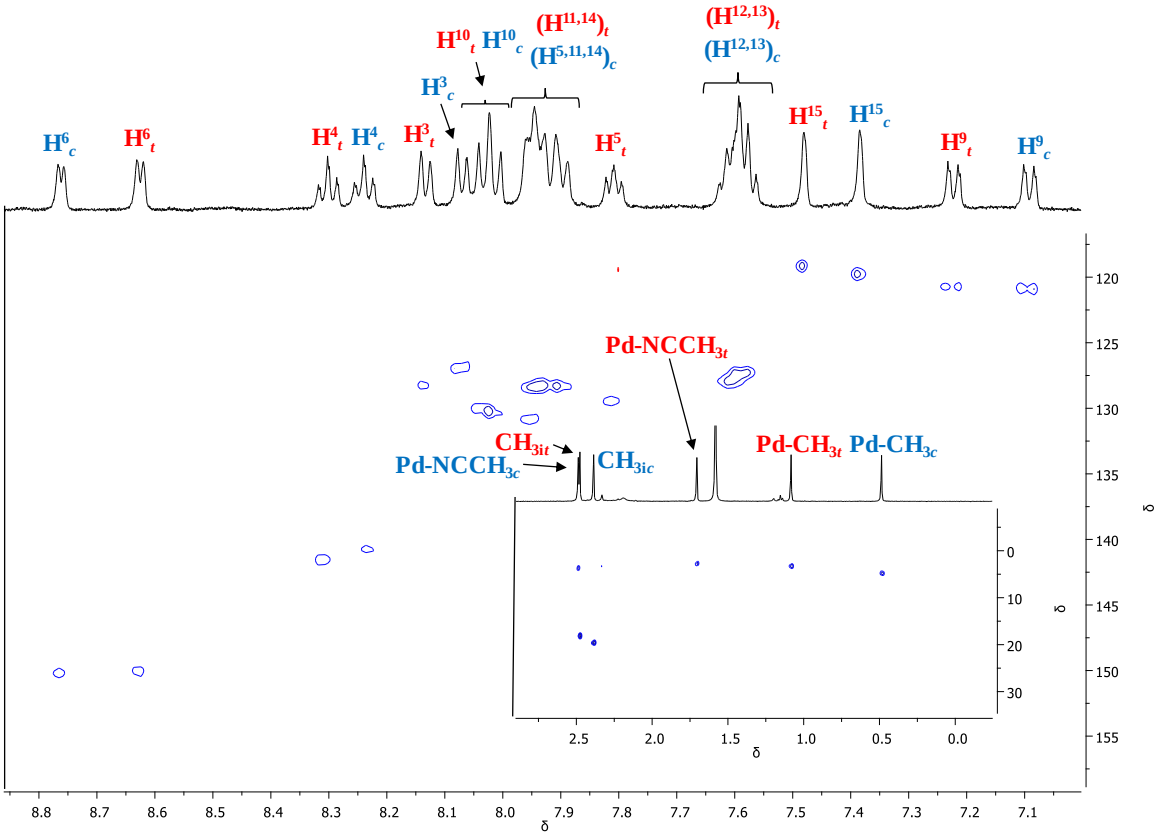

Figure S92. $^{1}H,^{13}C$-HSQC spectrum (CD_2Cl_2, T= 298 K) of **5b** (blue = CH/CH_3).

NMR characterization of [Pd(CH$_3$)(NCCH$_3$)(6)][PF$_6$] 6b (CD$_2$Cl$_2$, T = 298 K)

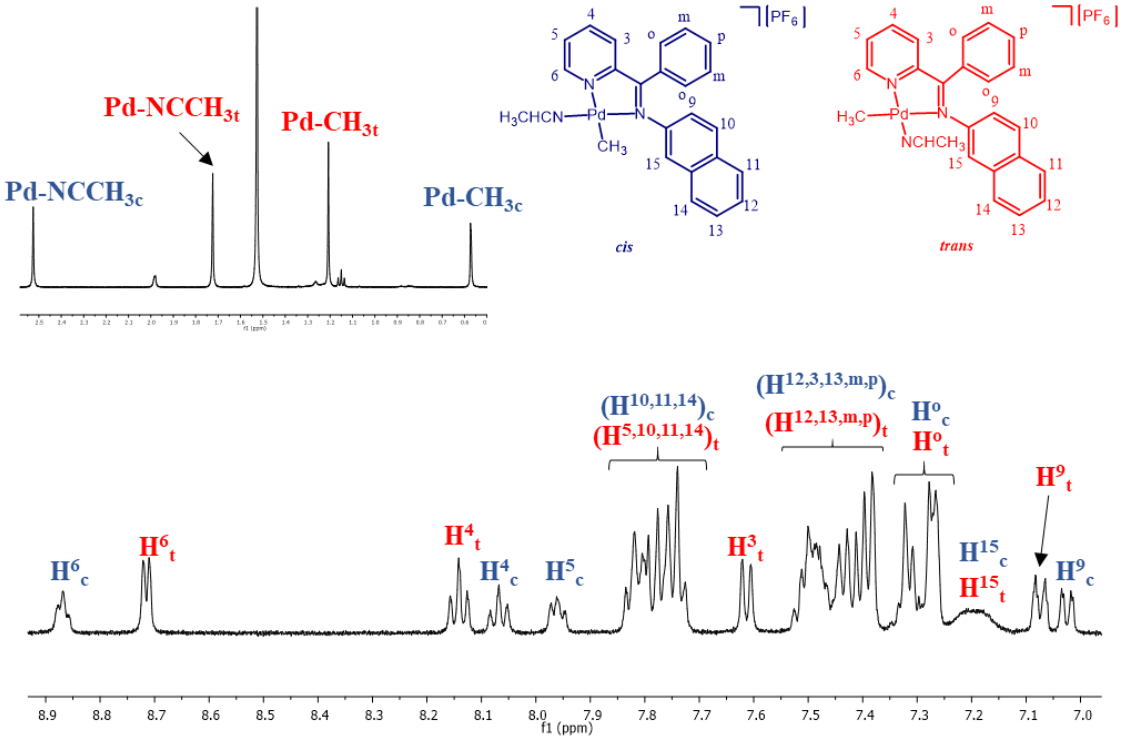

Figure S93. ^{1}H NMR spectrum (CD_2Cl_2, T = 298 K) of **6b**.

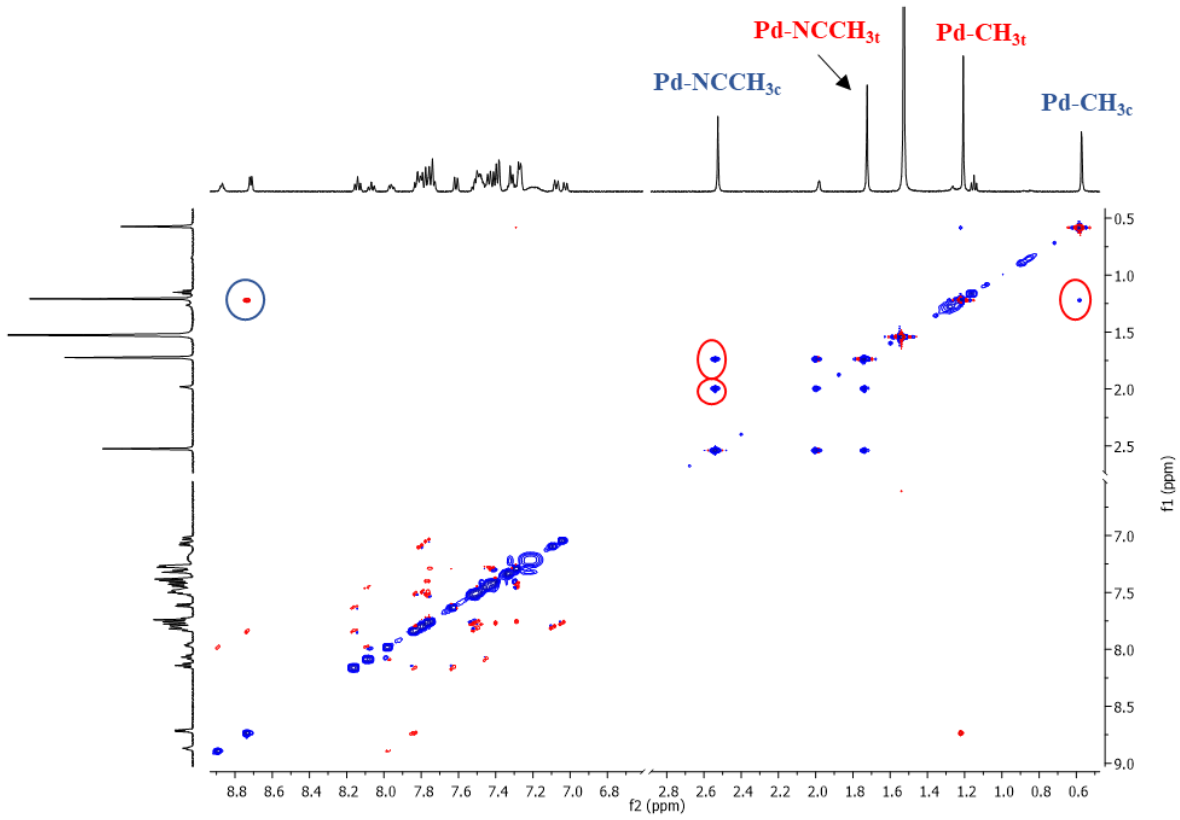

Figure S94. ^{1}H,^{1}H-NOESY spectrum (CD_2Cl_2, T = 298 K) of **6b**, (blue = exchange peaks, red = NOE peaks).

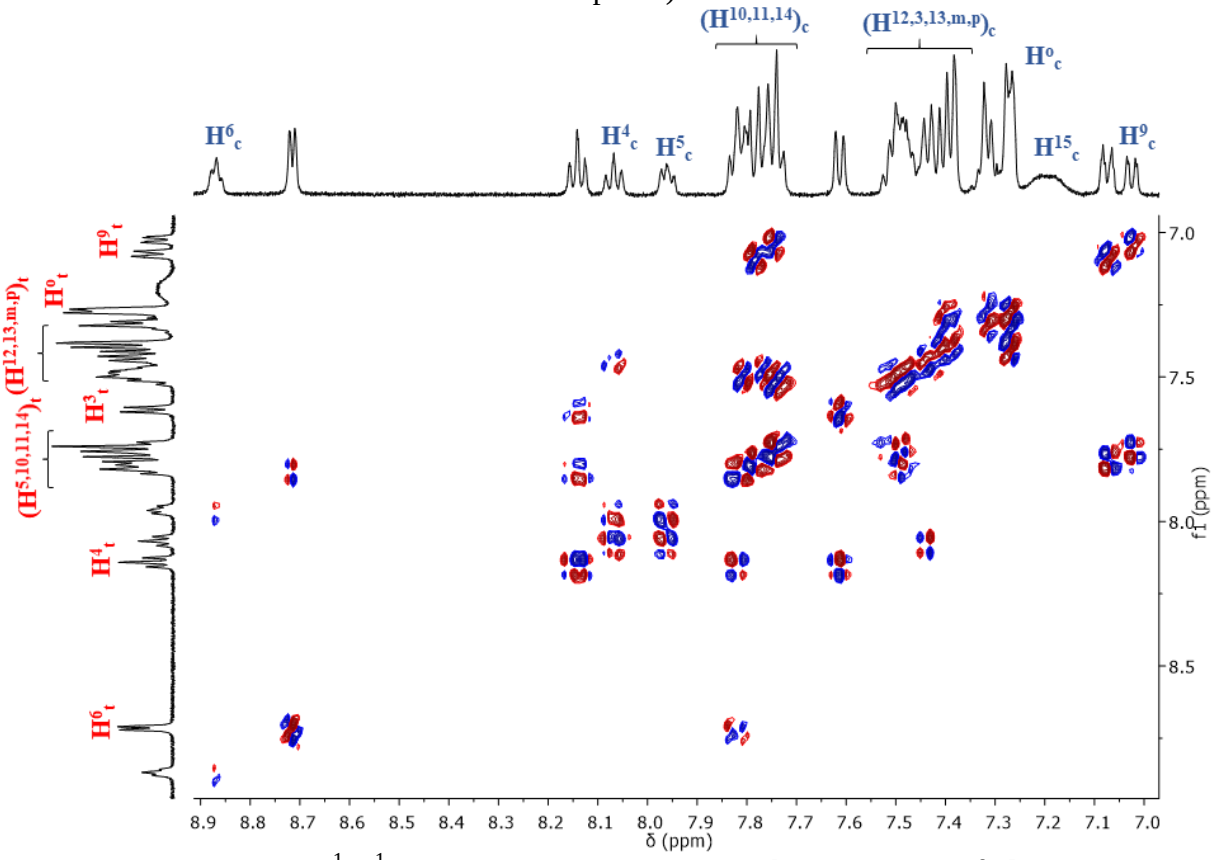

Figure S95. ^{1}H,^{1}H-DQCOSY spectrum (CD_2Cl_2, T = 298 K) of **6b**.

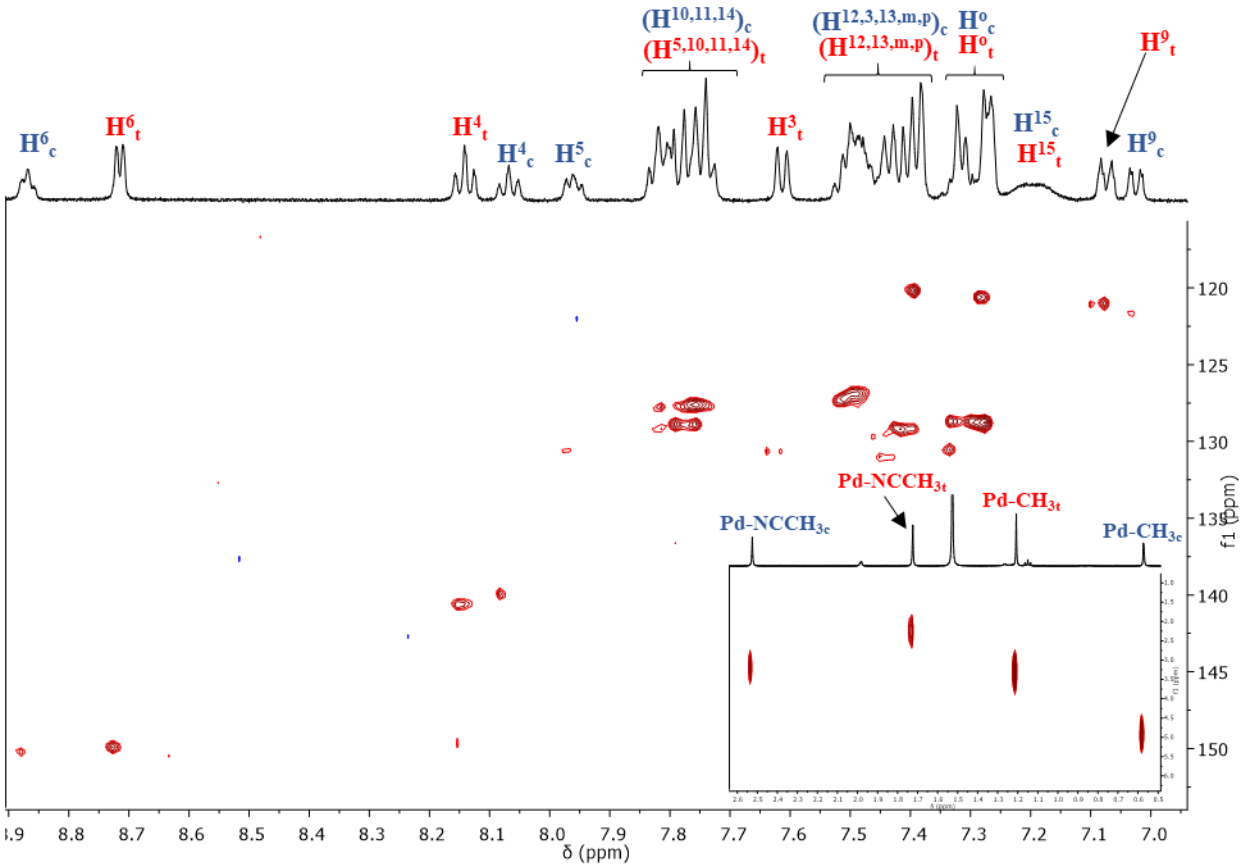

Figure S96. $^{1}H,^{13}C$-HSQC spectrum (CD_2Cl_2, T = 298 K) of **6b**.

NMR characterization of [Pd(CH$_3$)(NCCH$_3$)(7)][PF$_6$] 7b (CD$_3$NO$_2$, 273 K)

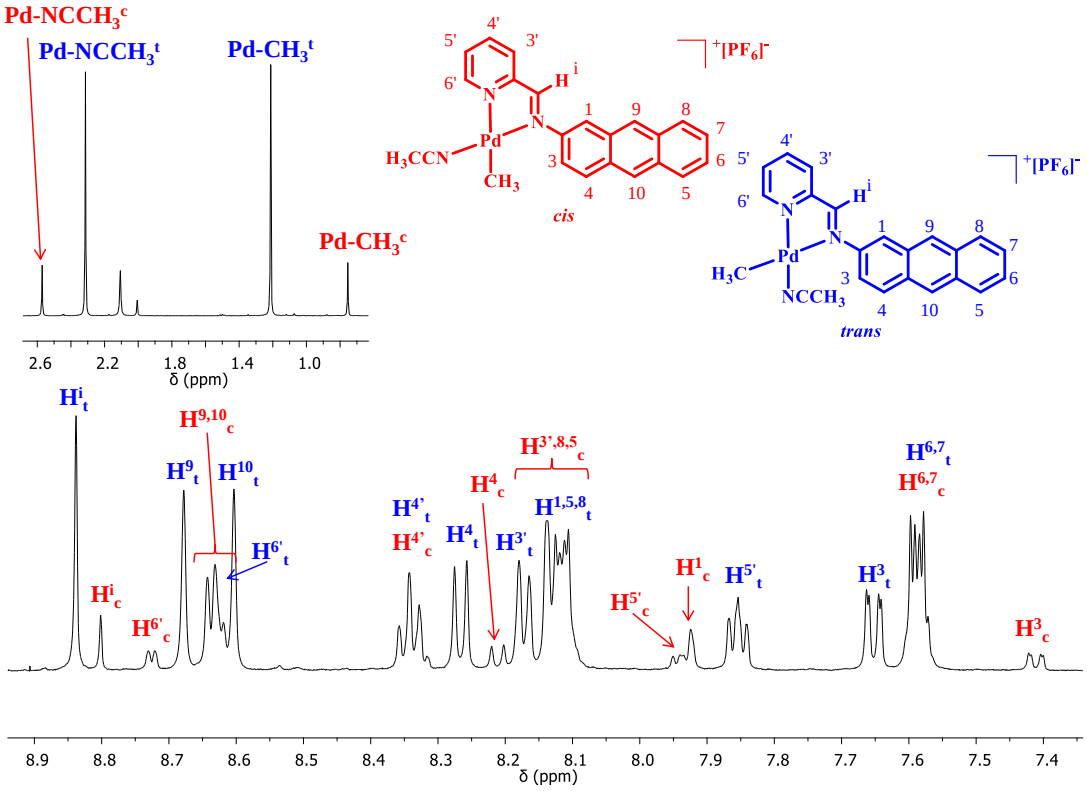

Figure S97. ^{1}H–NMR spectrum (CD_3NO_2, 273 K) of **7b**.

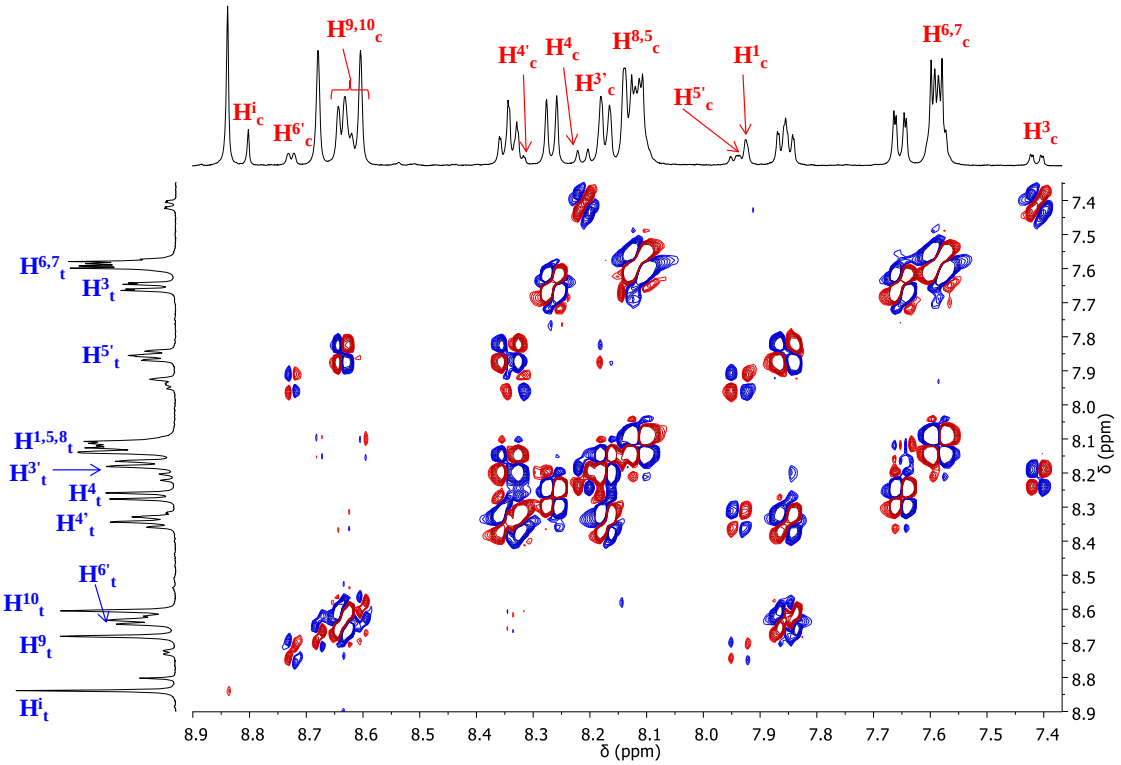

Figure S98. ^{1}H,^{1}H–DQCOSY spectrum (CD_3NO_2, 273 K) of **7b**, aromatic region.

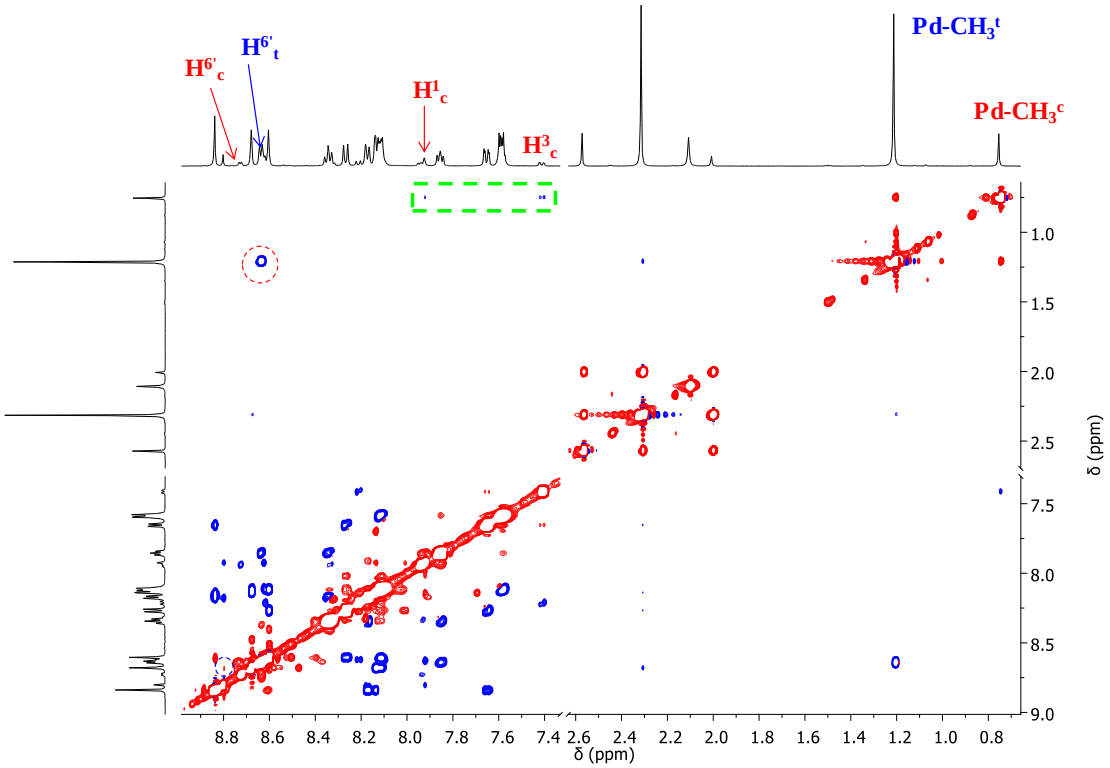

Figure S99. ^{1}H,^{1}H–NOESY spectrum (CD_3NO_2, 273 K) of **7b** (red = exchange peaks, blue = NOE peaks).

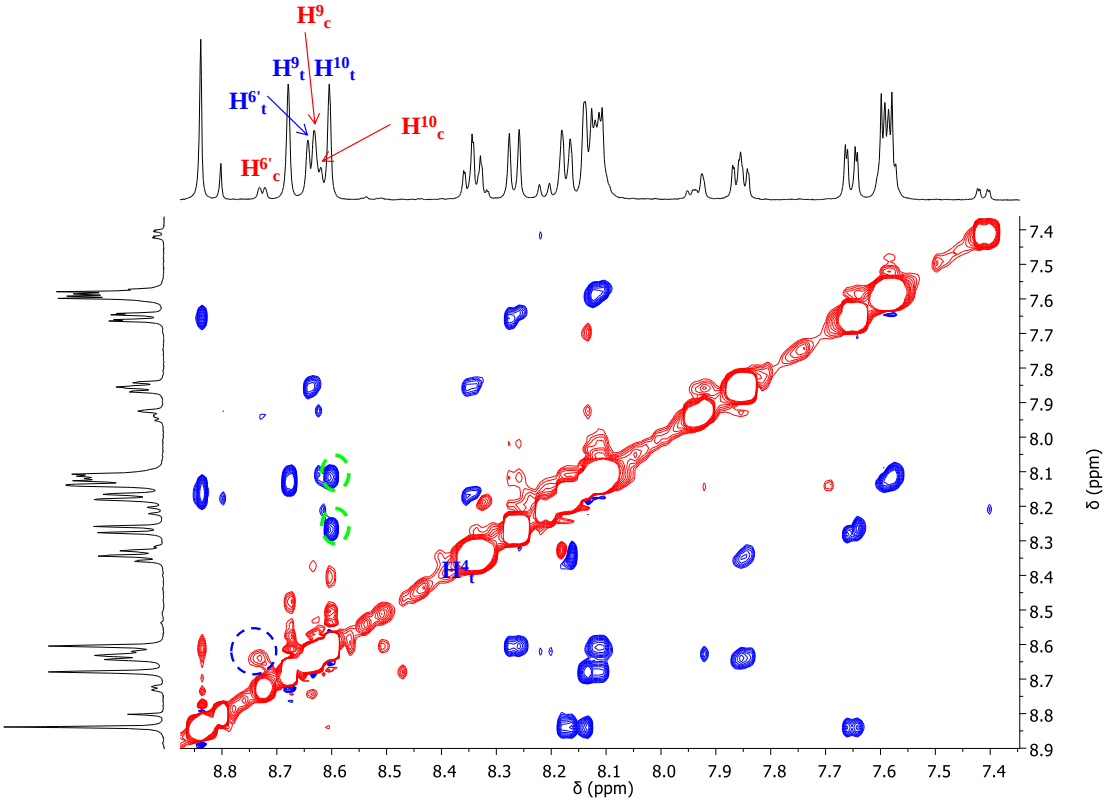

Figure S100. ^{1}H,^{1}H–NOESY spectrum (CD_3NO_2, 273 K) of **7b**, aromatic (region red = exchange peaks, blue = NOE peaks).

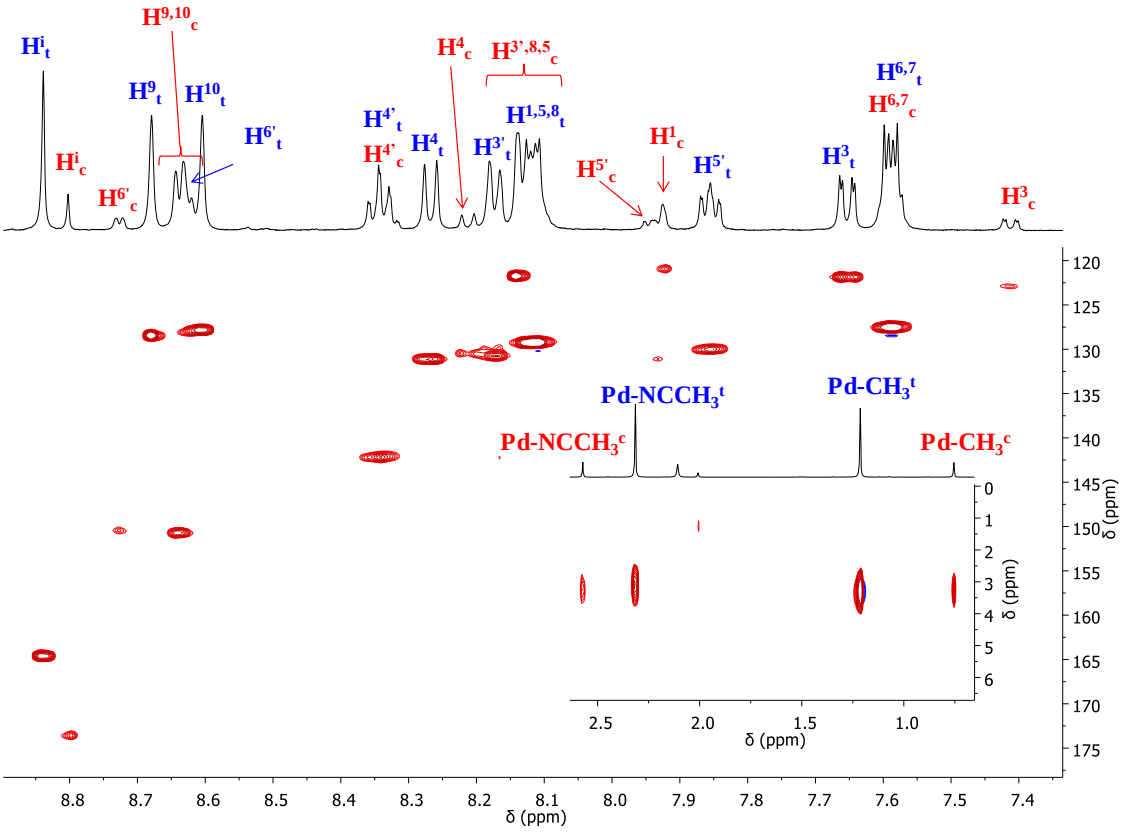

Figure S101. ^{1}H,^{13}C–HSQC spectrum (CD_3NO_2, 273 K) of **7b**.

NMR characterization of [Pd(CH$_3$)(NCCH$_3$)(8)][PF$_6$] 8b (CD$_3$NO$_2$, 273 K)

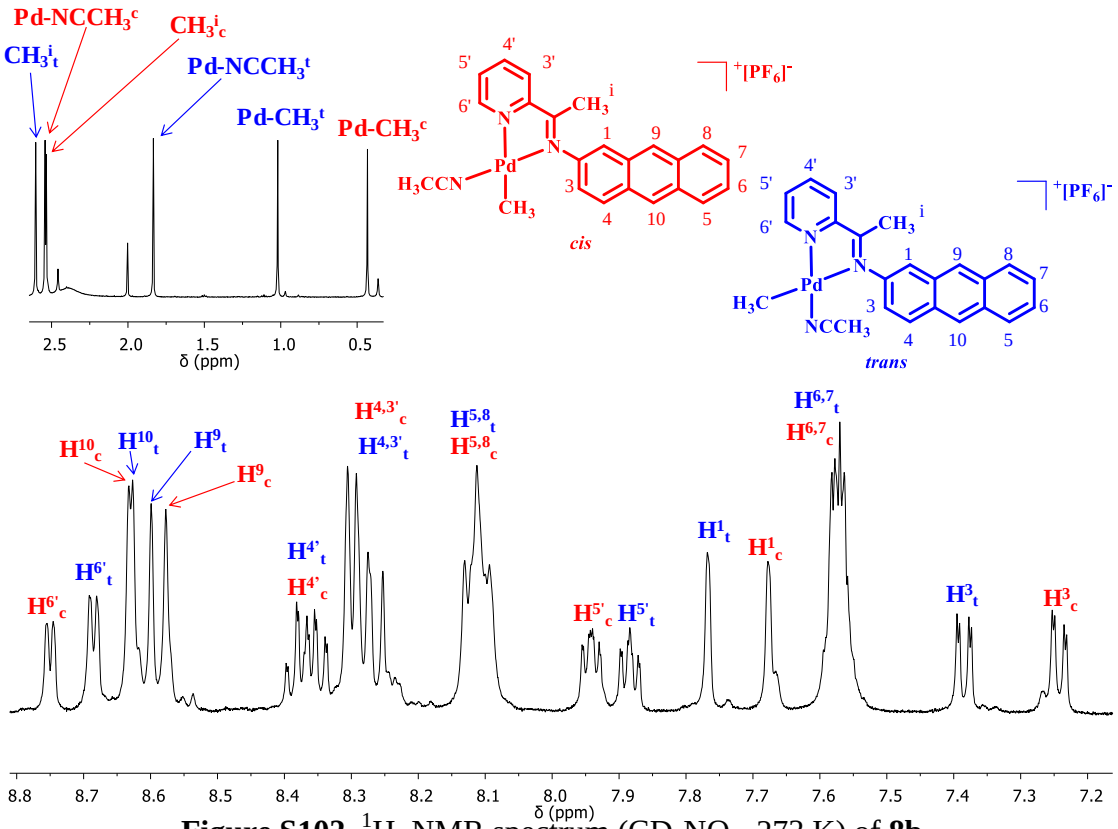

Figure S102. ^{1}H–NMR spectrum (CD$_3$NO$_2$, 273 K) of **8b**.

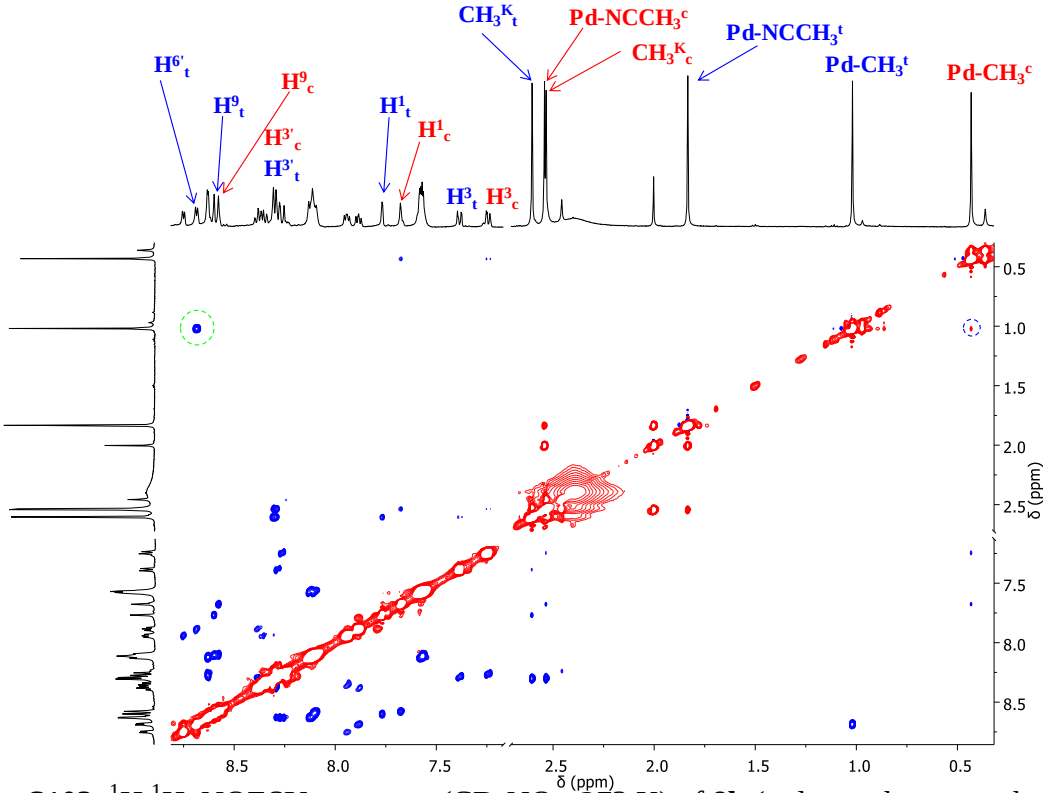

Figure S103. ^{1}H,^{1}H–NOESY spectrum (CD$_3$NO$_2$, 273 K) of **8b** (red = exchange peaks, blue = NOE peaks).

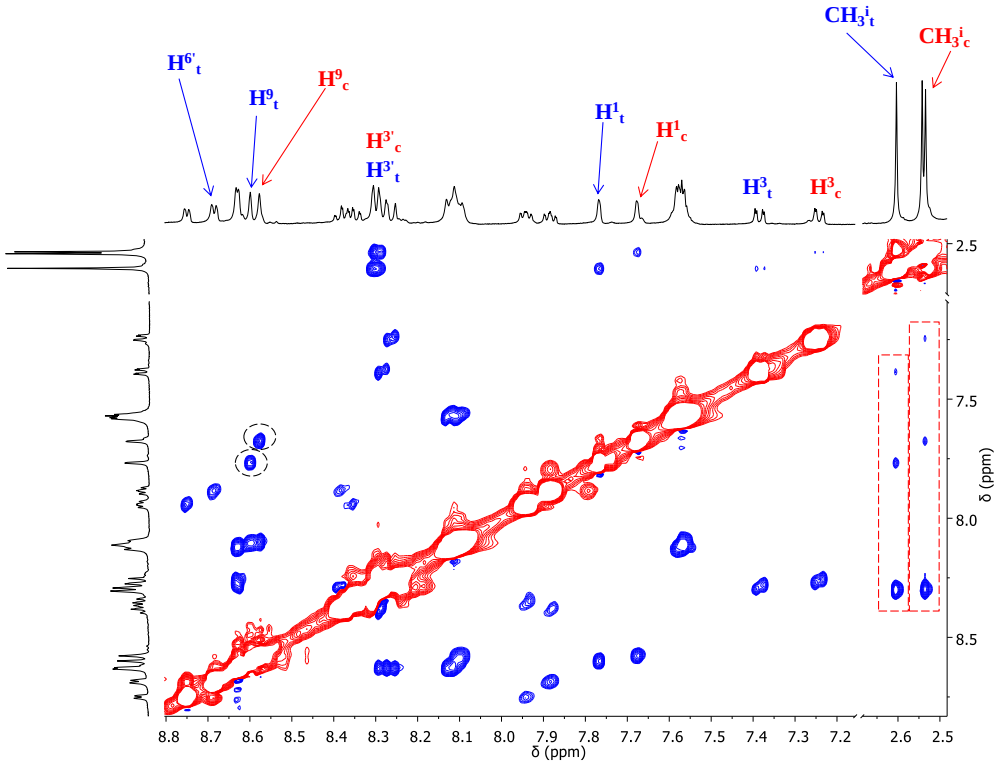

Figure S104. ^{1}H,^{1}H–NOESY spectrum (CD_3NO_2, 273 K) of **8b**, aromatic region (red = exchange peaks, blue = NOE peaks).

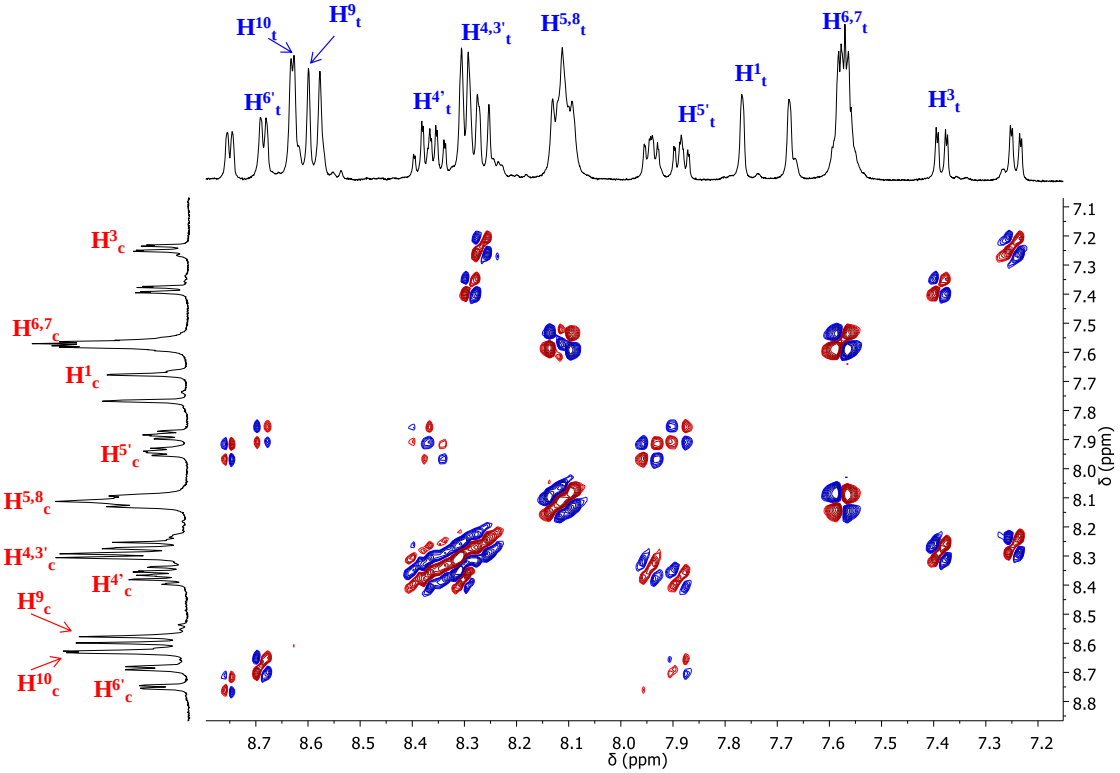

Figure S105. ^{1}H,^{1}H–DQCOSY (CD_3NO_2, 273 K) of **8b**.

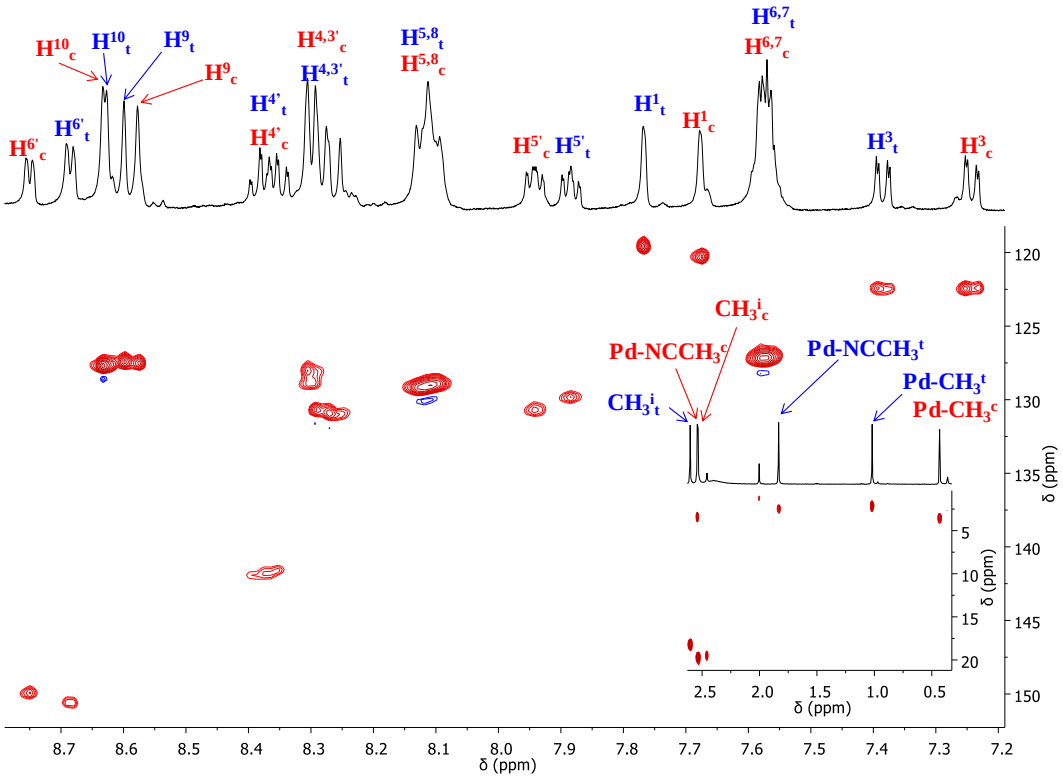

Figure S106. $^{1}H,^{13}C$–HSQC spectrum (CD_3NO_2, 273 K) of **8b** (red = CH/CH_3).

NMR characterization of [Pd(CH$_3$)(NCCH$_3$)(9)][PF$_6$] 9b (CD_2Cl_2, 298 K)

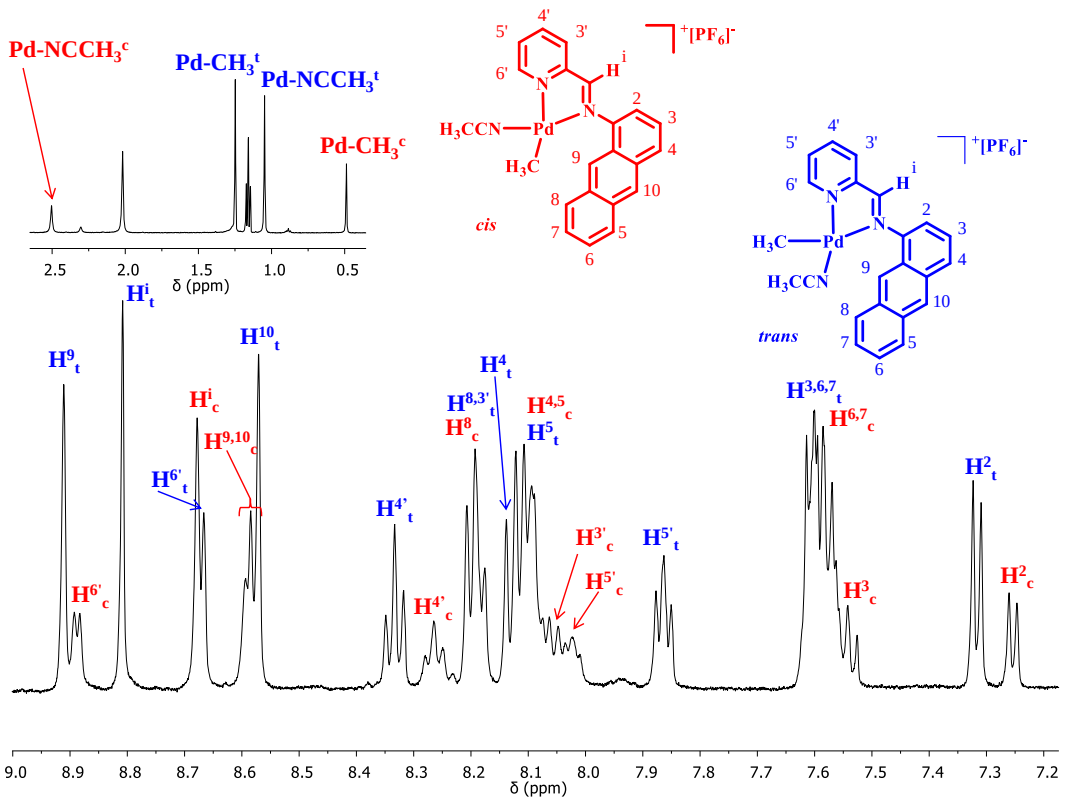

Figure S107. ^{1}H–NMR spectrum (CD_2Cl_2, 298 K) of **9b**.

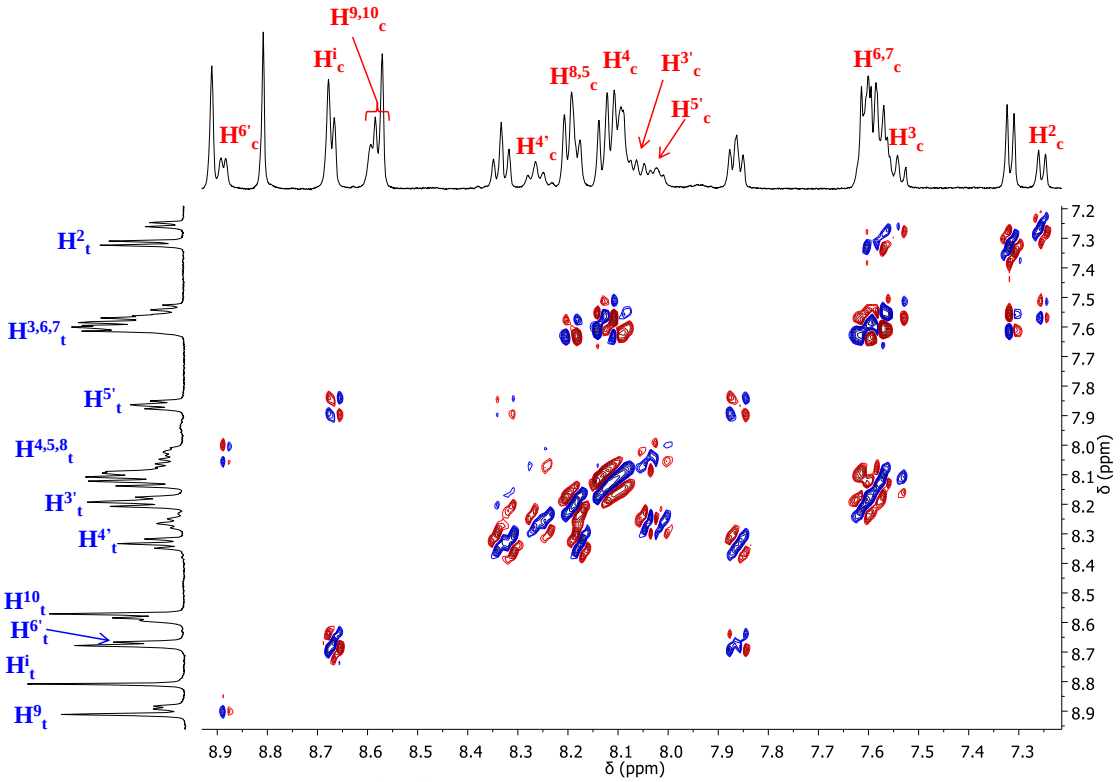

Figure S108. ^{1}H,^{1}H–DQCOSY spectrum (CD_2Cl_2, 298 K) of **9b**.

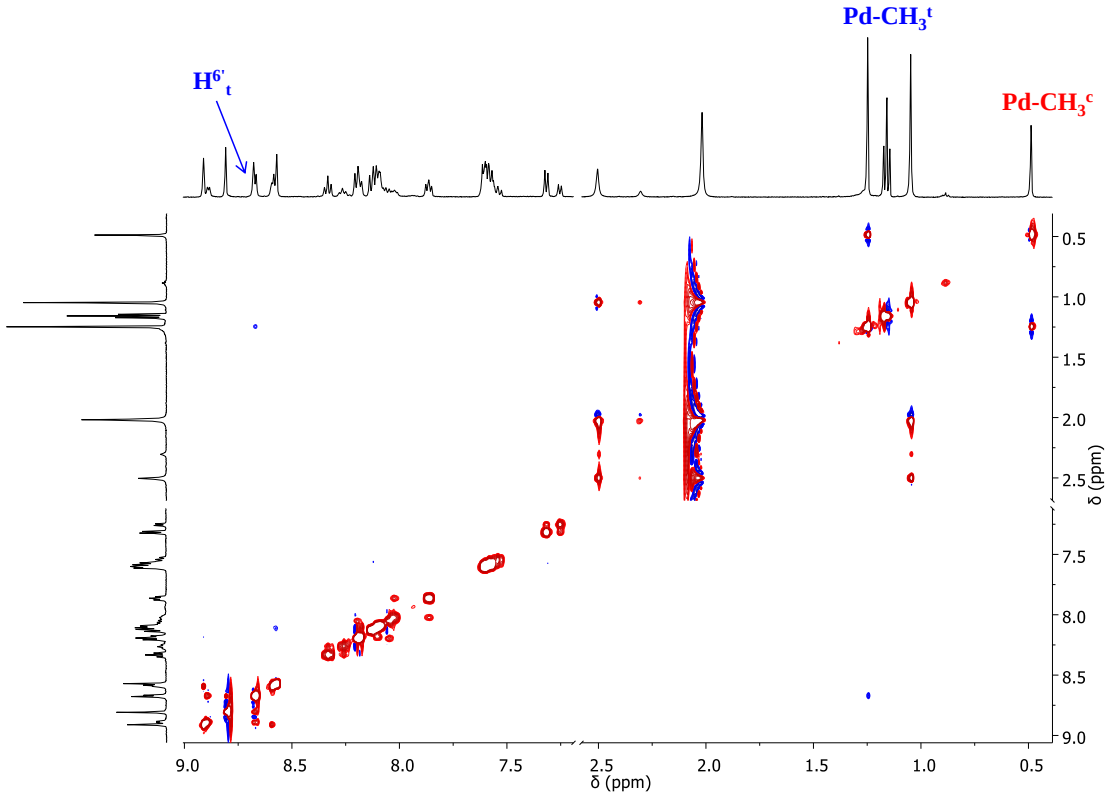

Figure S109. ^{1}H,^{1}H–NOESY spectrum (CD_2Cl_2, 298 K) of **9b** (red = exchange peaks, blue = NOE peaks).

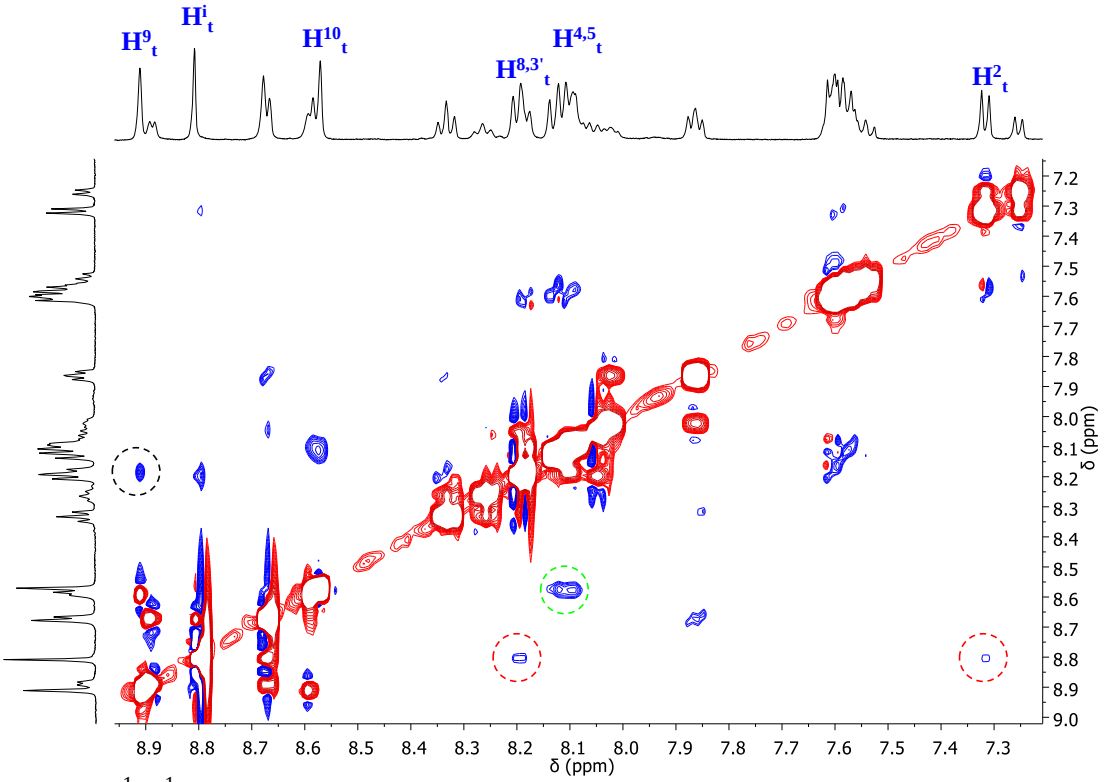

Figure S110. ^{1}H,^{1}H–NOESY spectrum (CD_2Cl_2, 298 K) of **9b**, aromatic region (red = exchange peaks, blue = NOE peaks).

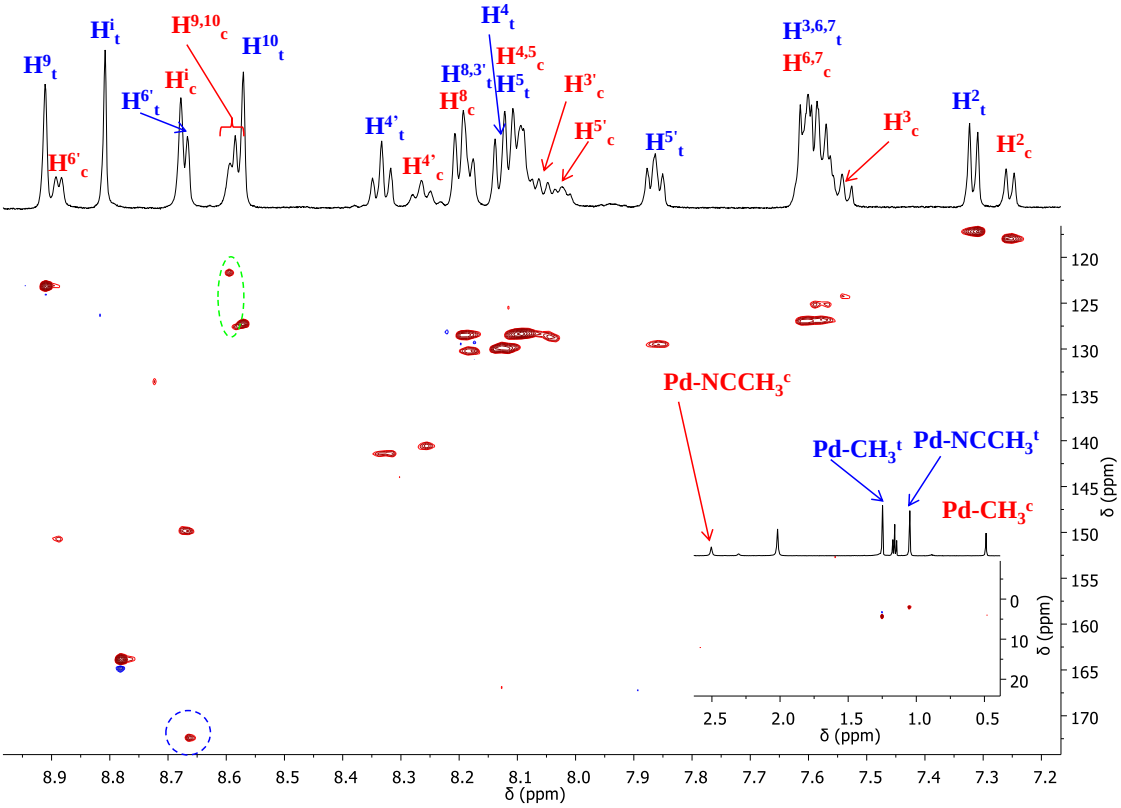

Figure S111. ^{1}H,^{13}C–HSQC spectrum (CD_2Cl_2, 298 K) of **9b** (red = CH/CH_3).

X-ray cristallography

Data collections for crystals of **1a**, **3a**, **4a**, **8a**, **9a** were performed at the X-ray diffraction beamline (XRD1) of the Elettra Synchrotron of Trieste (Italy) equipped with a Pilatus 2 M image plate detector. Collection temperature was 100 K (nitrogen stream supplied through an Oxford Cryostream 700); the wavelength of the monochromatic X-ray beam was 0.700 angstrom and the diffractograms were obtained with the rotating crystal method. The crystals were dipped in N-paratone and mounted on the goniometer head with a nylon loop. The diffraction data were indexed, integrated and scaled using the XDS code[3]. The structures were solved by the dual space algorithm implemented in the SHELXT code [4]. Fourier analysis and refinement were performed by the full-matrix least-squares methods based on F^2 implemented in SHELXL[5]. The Shelxle program was used for modeling [6]. Anisotropic thermal motion was allowed for all non- hydrogen atoms. Hydrogen atoms were placed at calculated positions with isotropic factors U = 1.2 × Ueq, where Ueq is the equivalent isotropic thermal factor of the bonded non hydrogen atom.

Data collection of **2a** was performed at ENSIACET, Université de Toulouse.

Crystal data and details of refinements are given in Table S1-S3.

References

[1] Dinda, J.; Sinha, C. "Naphthyl-(2-pyridylmethylene)amine complexes of silver(I) and ruthenium(II): synthesis, spectral studies and electrochemical behavior" Transition Metal Chemistry (2000) 28, 864-870.

[2] Köppl, A.; Alt, G. H. "Substituted 1-(2-pyridyl)-2-azaethene-(N,N)-nickel dibromide complexes as catalyst precursors for homogeneous and heterogeneous ethylene polymerization" J. Mol. Cat. A: Chem. (2000) 154, 45-43.

[3] Kabsch, W. Acta Cryst. D 66 (2010) 125-132.

[4] Sheldrick, G. M. "SHELXT - Integrated Space-Group and Crystal-Structure Determination". Acta Crystallogr., Sect. A: Found. Adv. (2015) 71, 3−8.

[5] Sheldrick, G.M. Acta Cryst. A64 (2008) 112-122.

[6] Huebschle, C. B.; Sheldrick, G. M.; Dittrich, B. "ShelXle: a Qt graphical user interface for SHELXL" J. Appl. Cryst., 44, (2011) 1281-1284.

Table S1. Most significant distances and angles for complexes **1a**, **2a**, **3a**, **4a**, **8a**, **9a**.

	***cis*-1a**	***cis*-2a**	***cis*-3a**	***trans*-4a**	***cis*-8a**	***trans*-9a**[a]
	Distance (Å)					
Pd-CH_3	2.027(2)	2.030(2)	2.047(1)	2.098(4)	2.032(2)	2.05(1)
Pd-Cl	2.2998(6)	2.3127(6)	2.3129(8)	2.298(1)	2.3064(6)	2.313(3)
Pd-N_{pyr}	2.132(1)	2.125(2)	2.129(1)	2.059(4)	2.131(2)	2.058(4)
Pd-N_{imm}	2.056(2)	2.057(2)	2.049(1)	2.151(4)	2.060(2)	2.152(5)
	Angle (°)					
CH_3-Pd-Cl	89.64(5)	88.65(7)	89.23(4)	87.8(1)	87.98(7)	87.4(3)
CH_3-Pd-N_{imm}	94.98(6)	96.45(9)	95.93(5)	173.4(2)	97.11(8)	171.3(3)
Cl-Pd-N_{imm}	175.36(4)	174.83(6)	174.76(3)	98.8(1)	174.77(4)	98.8(2)
CH_3-Pd-N_{pyr}	173.21(7)	174.22(9)	174.19(4)	94.2(2)	175.33(7)	95.0(3)
Cl-Pd-N_{pyr}	96.21(4)	96.91(6)	96.58(3)	177.5(1)	96.68(5)	174.3(2)
N_{imm}-Pd-N_{pyr}	79.21(5)	78.01(8)	78.26(4)	79.2(2)	78.25(6)	79.3(2)
Dihedral angle	69.24(4)	84.3(4)	78.62(4)	49.7(1)	70.64(4)	67.94(6)

[a] Values refer to the major population (71%) in which C_1 is trans to the anthracenyl group.

Table S2. X-ray diffraction data for complexes **1a - 4a**.

Compound	1a	2a	3a	4a
Formula	$C_{17}H_{15}ClN_2Pd$, ½ CH_2Cl_2	$C_{18}H_{17}Cl\ N_2Pd$	$C_{23}H_{19}ClN_2Pd$	$C_{17}H_{15}ClN_2Pd$, CH_2Cl_2
Formula weight (Da)	389.19	403.19	465.25	389.19
Temperature (K)	173(2)	180(2)	173(2)	173(2)
Wavelength (Å)	0.700	0.71073	0.700	0.700
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space Group	P 21/c	P 21/c	P 21/n	P 21 21 21
a (Å)	11.839 (1)	12.9481(5)	8.491(5)	7.52(1)
b (Å)	9.790(2)	12.0822(3)	20.059(4)	12.357(4)
c (Å)	15.847(2)	11.1080(5)	11.5570(6)	19.840(5)
alpha (deg)	90	90	90	90
beta (deg)	111.70(1)	114.126(5)	94.89(2)	90
gamma (deg)	90	90	90	90
V ($Å^3$)	1706.6(5)	1586.0(1)	1961 (1)	1843(3)
Z	4	4	4	4
rho (g cm^{-3})	1.680	1.689	1.576	1.709
F(000)	860	808	936	944
mu (mm^{-1})	1.324	1.335	1.034	1.366
theta min,max(deg)	2.660,28.647	3.37,27.48	2.008,28.227	1912,28.649
Resolution (Å)	0.73	0.73	0.74	0.73
Total refl. collctd	82642	33226	62725	30973
Independent refl.	4553	3625	4935	4908
Obs. Refl. $F_o>4\sigma_{Fo}$	4553	3016	4881	4710
I/sigma(I) (all data)	82.83	31.76	79.60	24.54
I/sigma (I) (max resltn)	74.73	22.54	61.86	17.85
Rmerge (all data)	3.3%	3.6%	3.4%	7.7%
Rmerge (max resltn)	2.9%	5.2%	3.7%	11.6%
Completeness (all data)	0.985	0.997	0.959	0.983
Multiplicity (all data)	17.6	9.2	12.5	11.0
Multiplicity (max resltn)	17.6	7.8	12.1	10.9
Data/restraint/parameters	4553/2/218	3625/0/201	4935/21/301	4908/0/218
$R_{I>2\sigma I}$,$wR_{2,I>2\sigma I}$	0.0240,0.0662	0.0261,0.0509	0.0186,0.0568	0.0338,0.849
R (all data), wR_2 (all data)	0.0240,0.0662	0.0378,0.0551	0.0187,0.0570	0.0358,0.0860
GooF	1.127	1.048	1.095	1.062

Table S3. X-ray diffraction data for complexes **8a**, **9a**.

Compound	8a	9a
Formula	$C_{22}H_{19}ClN_2Pd$	$C_{21}H_{17}ClN_2Pd$, CH_2Cl_2
Formula weight (Da)	453.27	439.25
Temperature (K)	173(2)	100(2)
Wavelength (Å)	0.700	0.700
Crystal system	Orthorhombic	monoclinic
Space Group	P b c a	P 21/n
a (Å)	8.939(4)	11.747(5)
b (Å)	10.62(2)	8.750(5)
c (Å)	38.547(5)	20.833(3)
alpha (deg)	90	90
beta (deg)	90	103.80(1)
gamma (deg)	90	90
V ($Å^3$)	3659(1)	2079(2)
Z	1	4
rho ($g\ cm^{-3}$)	1.646	1.674
F(000)	1824	1048
mu (mm^{-1})	1.106	1.219
theta min,max(deg)	1.041,29.083	1.801,28.222
Resolution (Å)	0.72	0.74
Total refl. collctd	61073	29189
Independent refl.	5031	4995
Obs. Refl. $F_o>4\sigma_{Fo}$	5004	4906
I/sigma(I) (all data)	22.05	32.63
I/sigma (I) (max resltn)	20.09	22.30
Rmerge (all data)	8.9%	3.4%
Rmerge (max resltn)	7.7%	5.3%
Completeness (all data)	0.973	0.922
Multiplicity (all data)	11.6	5.7
Multiplicity (max resltn)	11.4	5.6
Data/restraint/parameters	5031/6/245	4995/3/257
$R_{I>2\sigma I}$,$wR_{2,I>2\sigma I}$	0.0361,0.1052	0.0422,0.1124
R (all data), wR_2 (all data)	0.0362,0.1053	0.0428,0.1129
GooF	1.011	1.047

Characterization of the synthesized polyketones

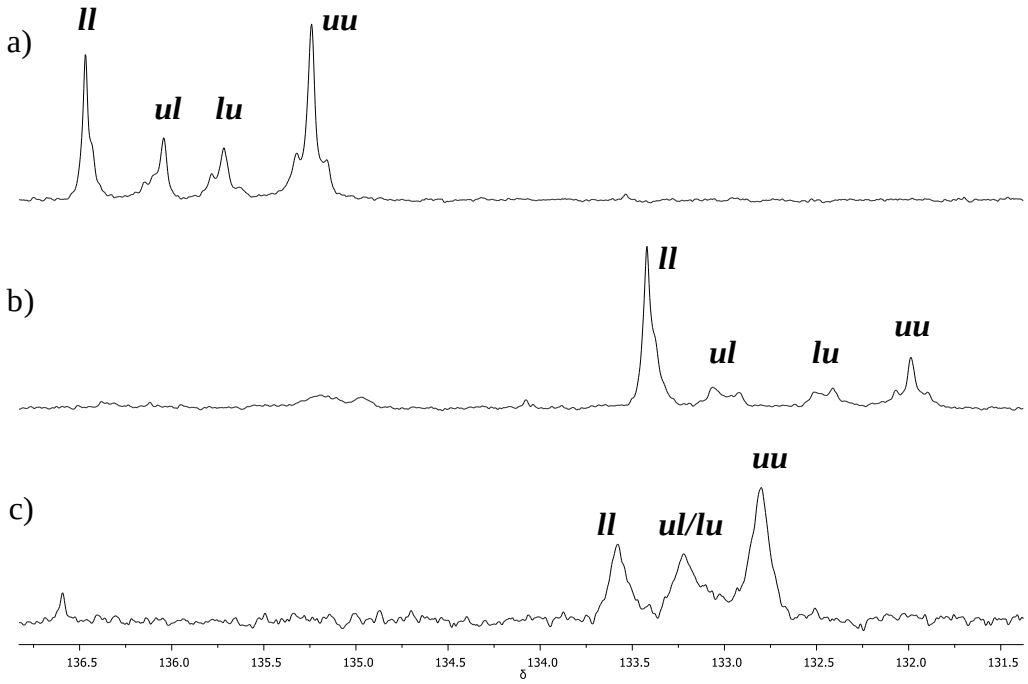

Figure S112. ^{13}C NMR spectrum (HFIP/$CDCl_3$, T = 298 K) of a) CO/styrene, b) CO/4-methylstyrene, c) 4-*tert*-butyl styrene copolymers obtained with **1b**; *ipso* carbon atom region.

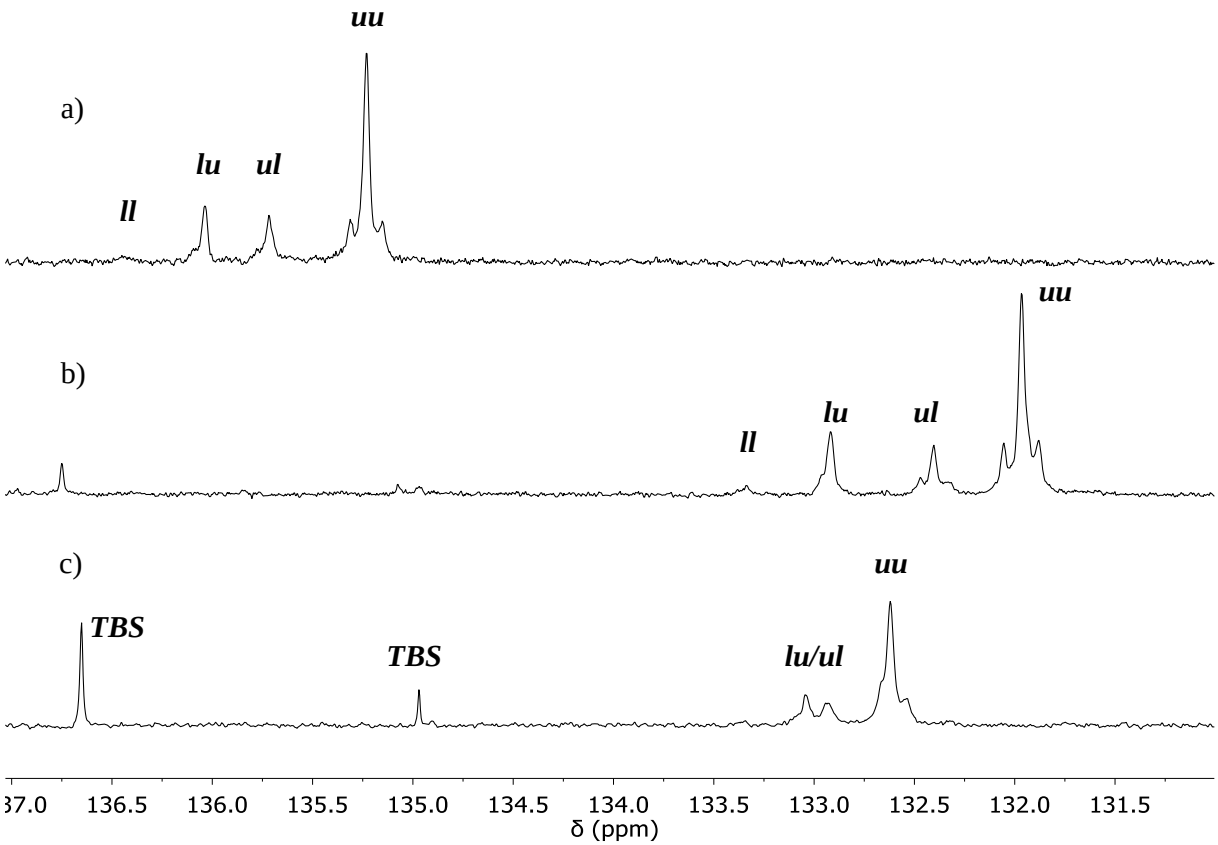

Figure S113. ^{13}C NMR spectrum (HFIP/$CDCl_3$, T = 298 K) of a) CO/styrene, b) CO/4-methylstyrene, c) 4-*tert*-butyl styrene copolymers obtained with **2b**; *ipso* carbon atom region.

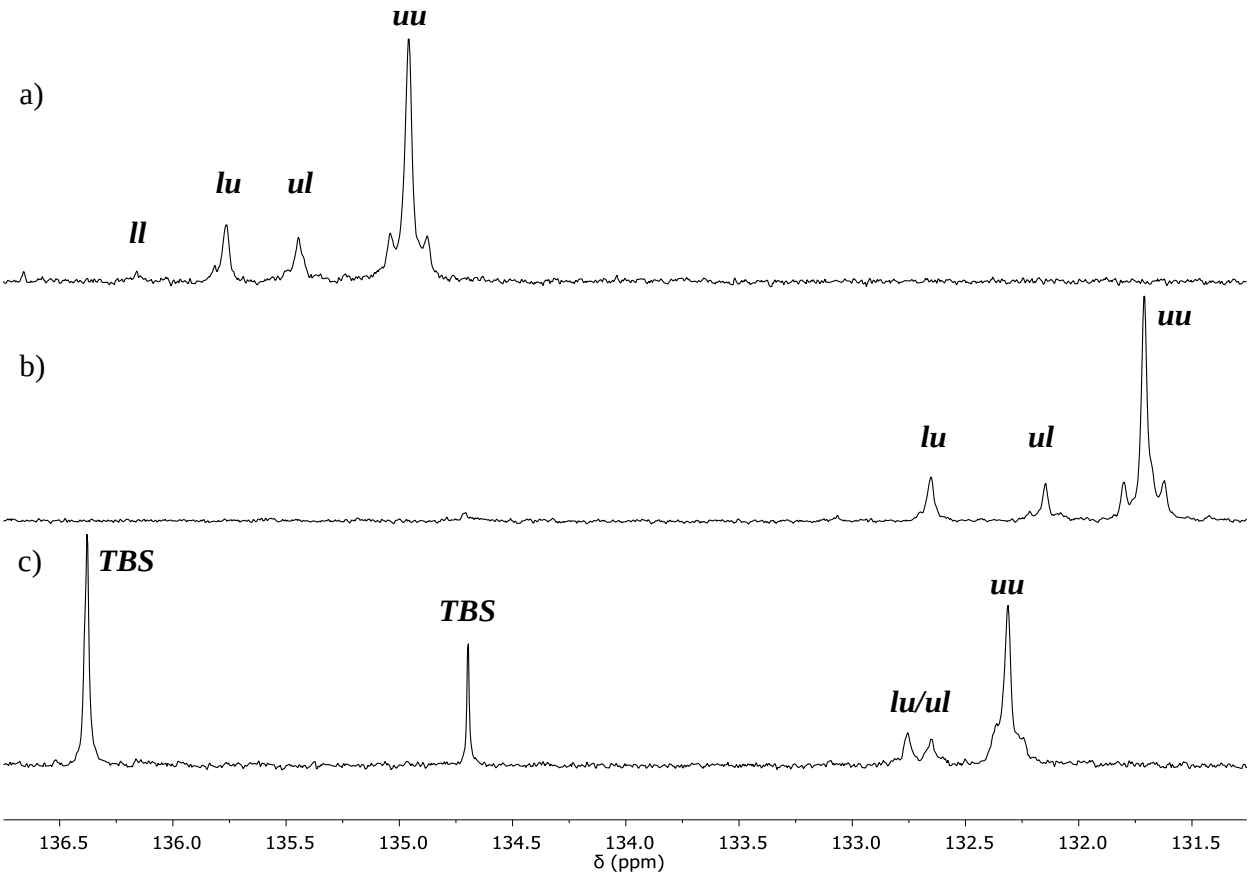

Figure S114. ^{13}C NMR spectrum (HFIP/$CDCl_3$, T = 298 K) of a) CO/styrene, b) CO/4-methylstyrene, c) 4-*tert*-butyl styrene copolymers obtained with **3b**; *ipso* carbon atom region.

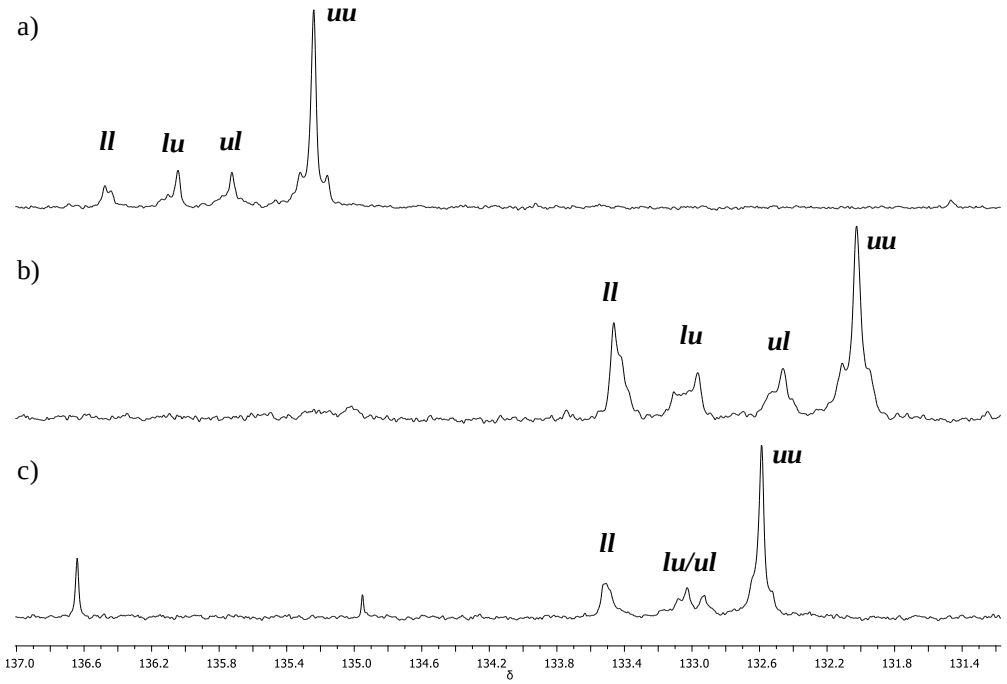

Figure S115. ^{13}C NMR spectrum (HFIP/$CDCl_3$, T = 298 K) a) CO/styrene, b) CO/4-methyl styrene, c) 4-*tert*-butyl styrene copolymers obtained with **4b**; *ipso* carbon atom region.

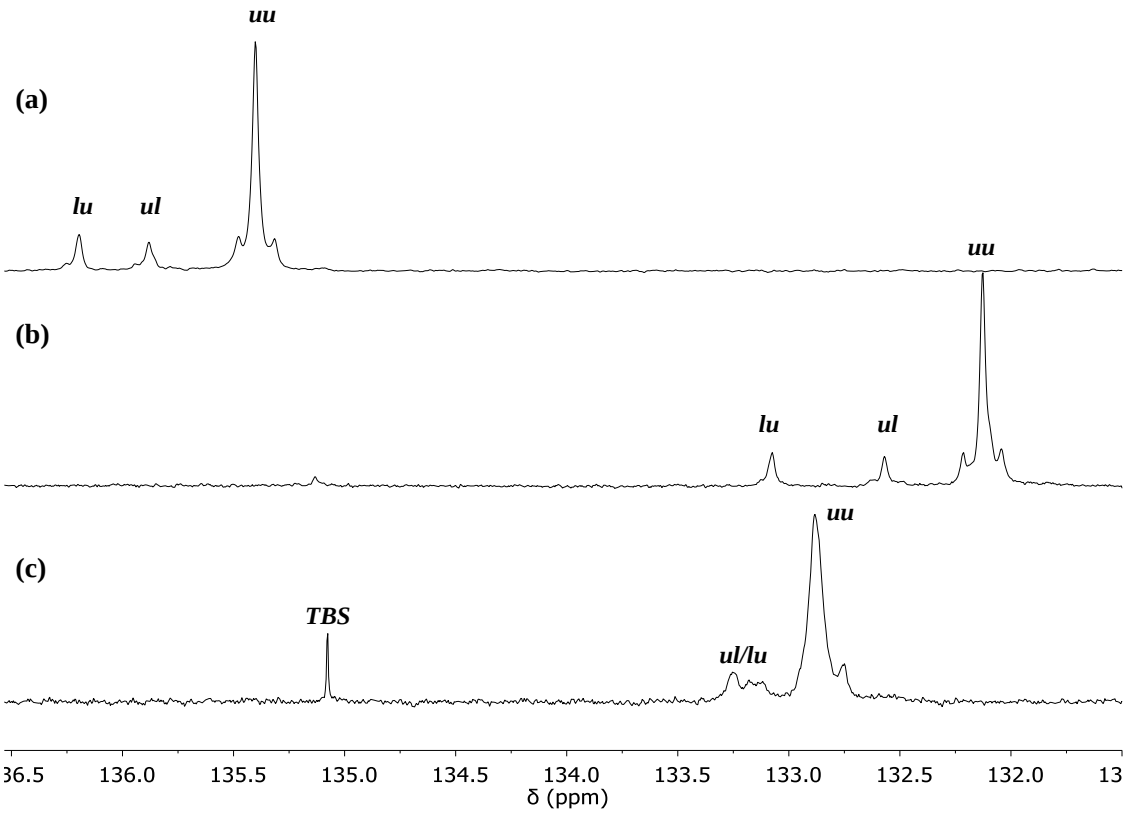

Figure S116. ^{13}C NMR spectrum (HFIP/$CDCl_3$, T = 298 K) of a) CO/styrene, b) CO/4-methylstyrene, c) 4-*tert*-butyl styrene copolymers obtained with **5b**; *ipso* carbon atom region.

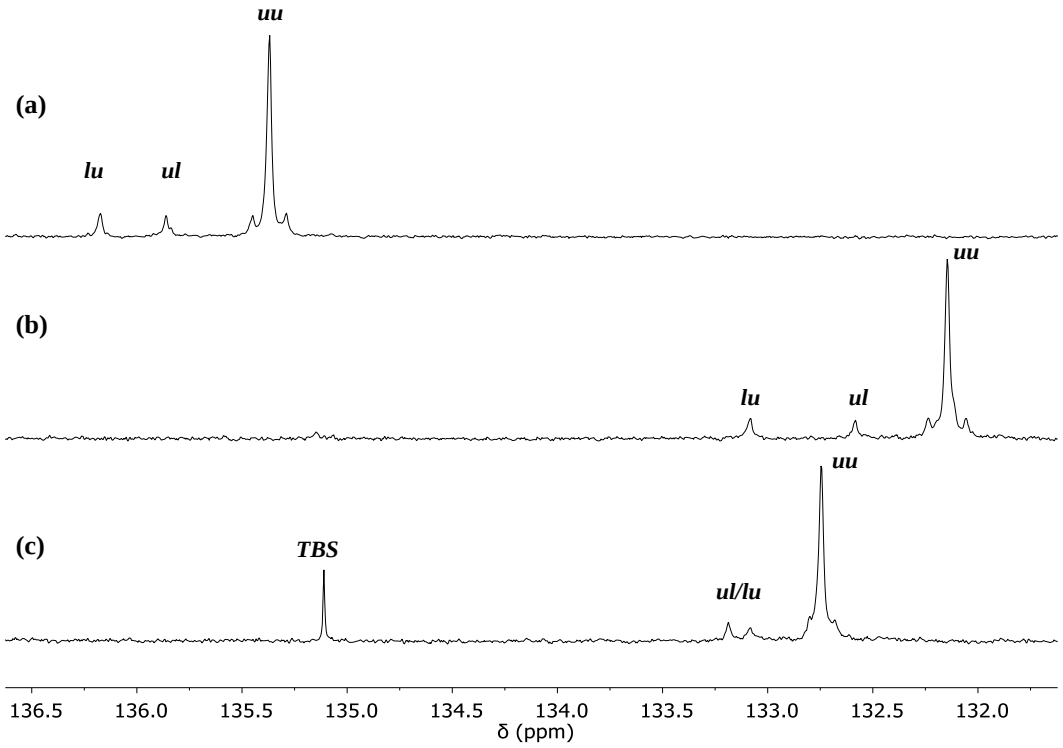

Figure S117. ^{13}C NMR spectrum (HFIP/$CDCl_3$, T = 298 K) of a) CO/styrene, b) CO/4-methylstyrene, c) 4-*tert*-butyl styrene copolymers obtained with **6b**; *ipso* carbon atom region.

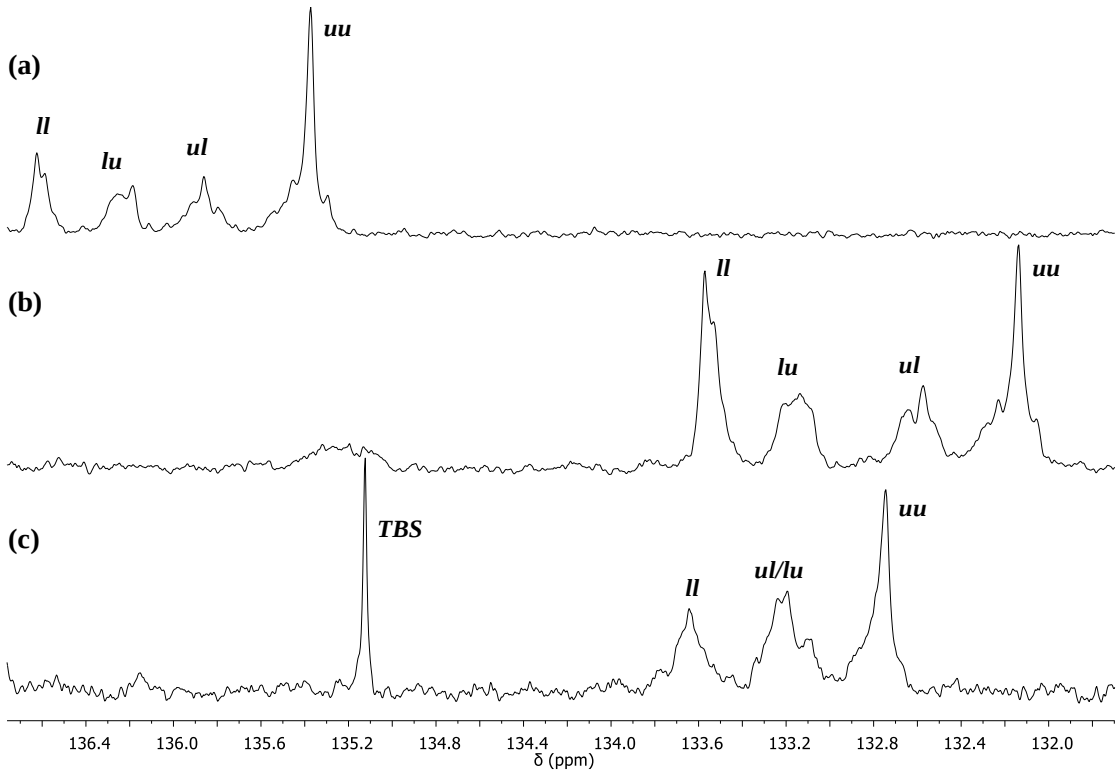

Figure S118. ^{13}C NMR spectra (HFIP/$CDCl_3$ = 1:2, T = 298 K) of a) CO/S, b) CO/MS, c) CO/TBS obtained with **7b**; *ipso* carbon atom region.

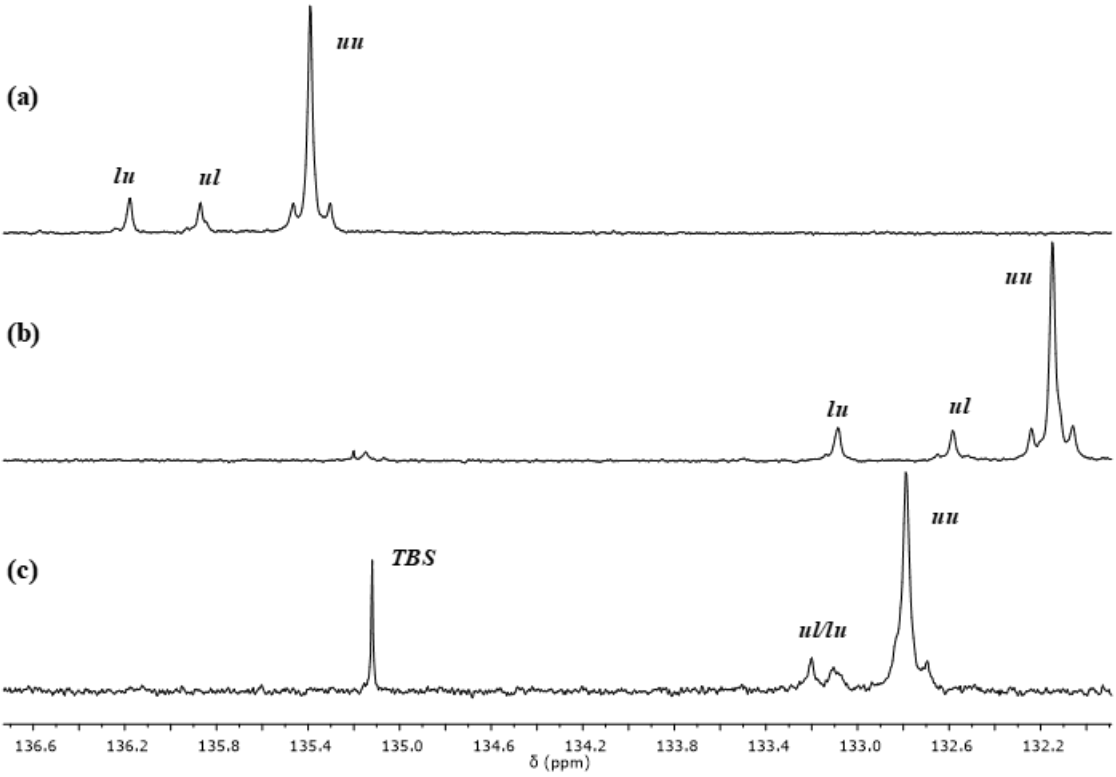

Figure S119. ^{13}C NMR spectra (HFIP/$CDCl_3$ = 1:2, T = 298 K) of a) CO/S, b) CO/MS, c) CO/TBS obtained with **8b**; *ipso* carbon atom region.

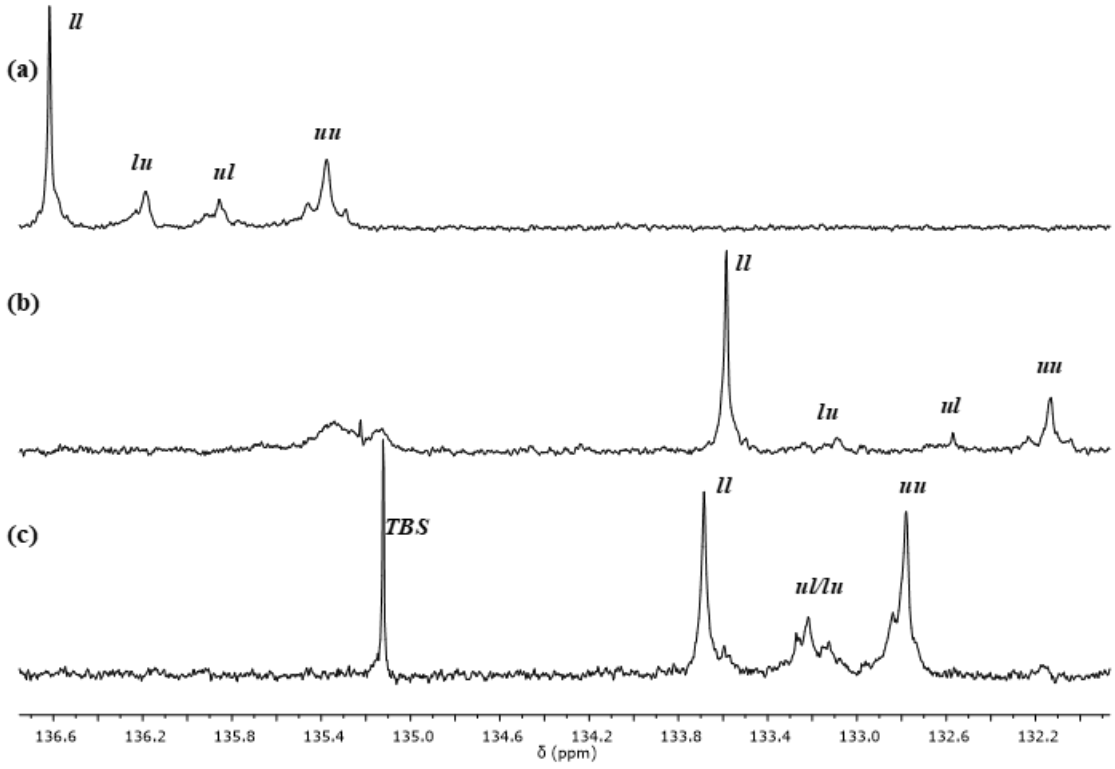

Figure S120. ^{13}C NMR spectra (HFIP/$CDCl_3$ = 1:2, T = 298 K) of a) CO/S, b) CO/MS, c) CO/TBS obtained with **9b**; *ipso* carbon atom region.

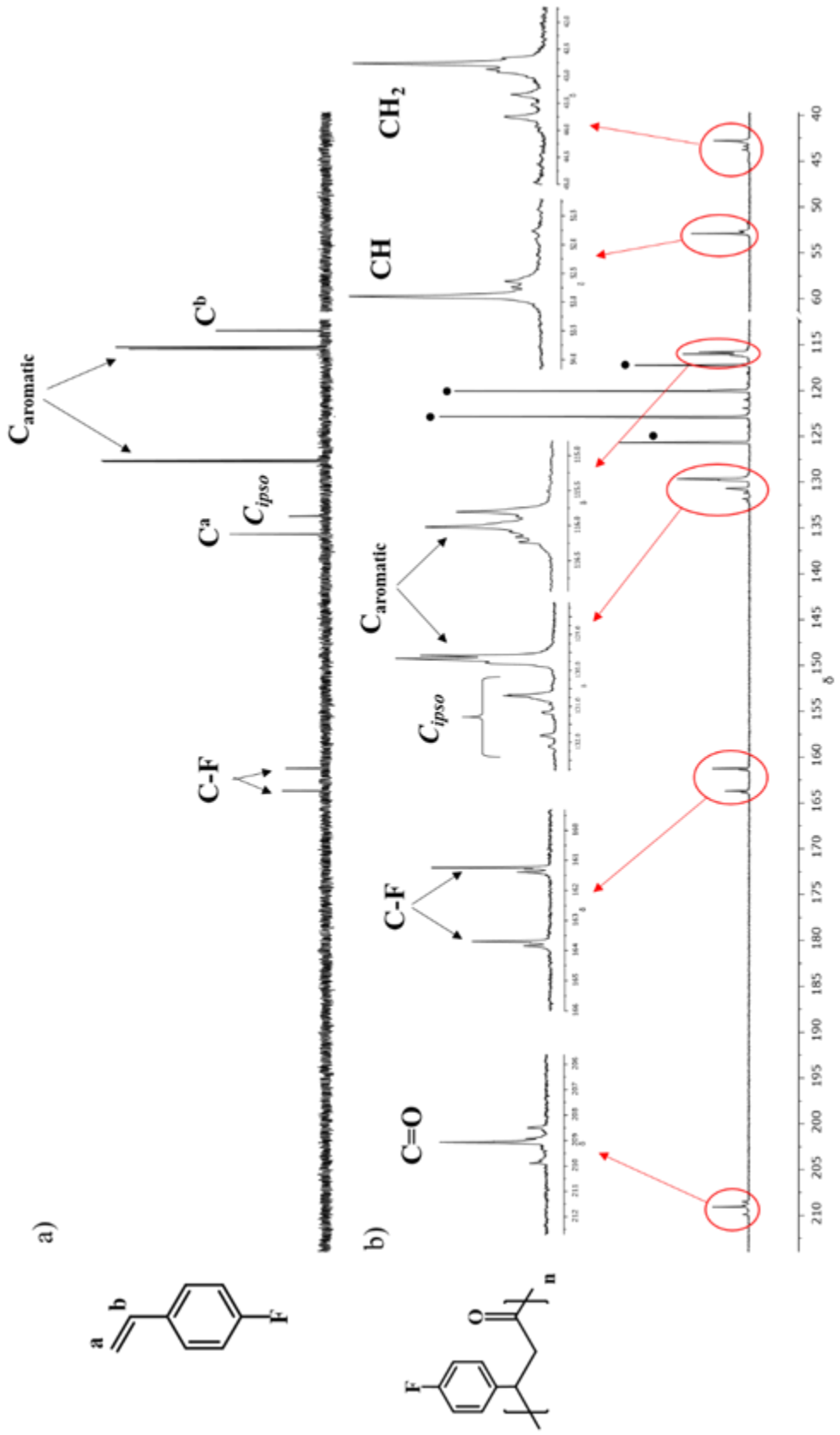

Figure S121. ^{13}C NMR spectrum ($CDCl_3$/HFIP, T = 298 K) of: (a) CO/FS copolymer obtained with **4b**; (b) 4-fluorostyrene.

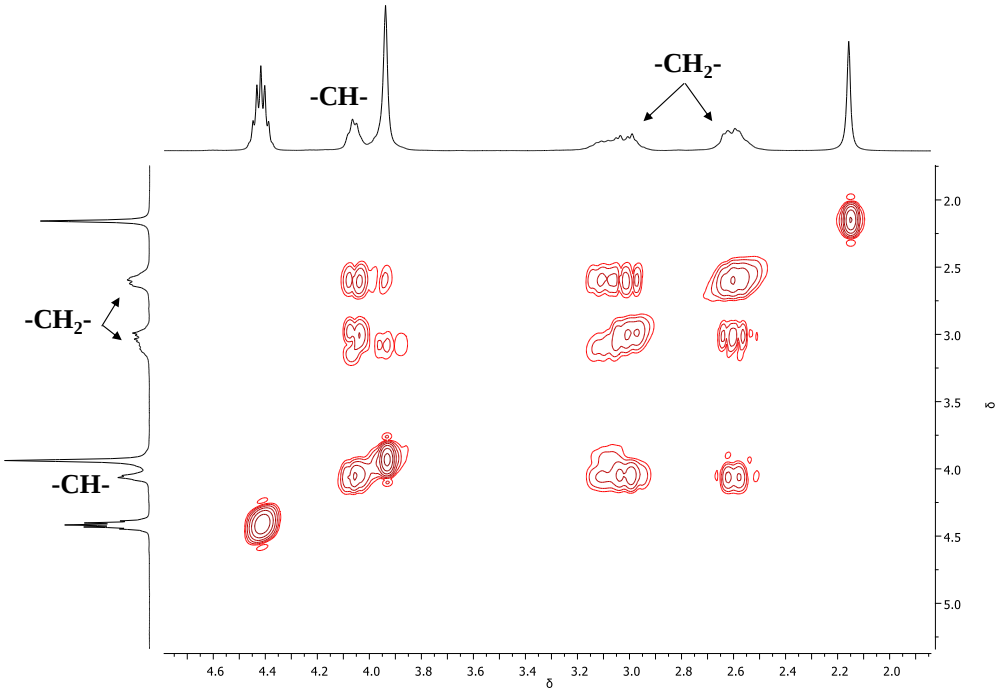

Figure S122. $^{1}H,^{1}H$-COSY spectrum ($CDCl_3$/HFIP, T = 298 K) of CO/FS copolymer obtained with **4b**.

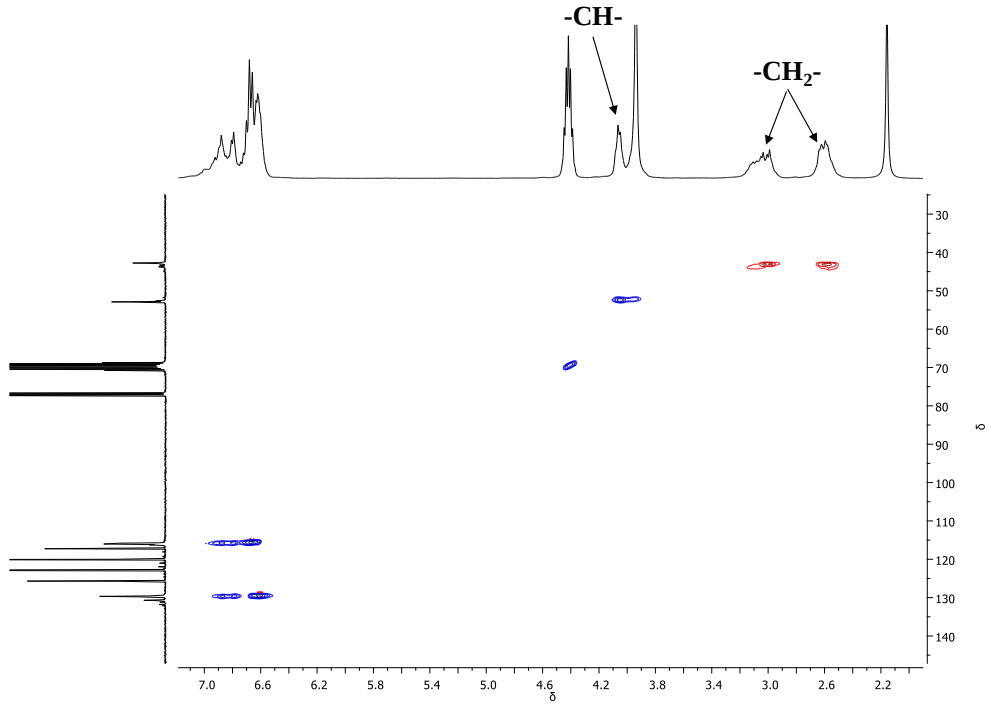

Figure S123. $^{1}H,^{13}C$-HSQC spectrum ($CDCl_3$/HFIP, T = 298 K) of CO/FS copolymer obtained with **4b**.

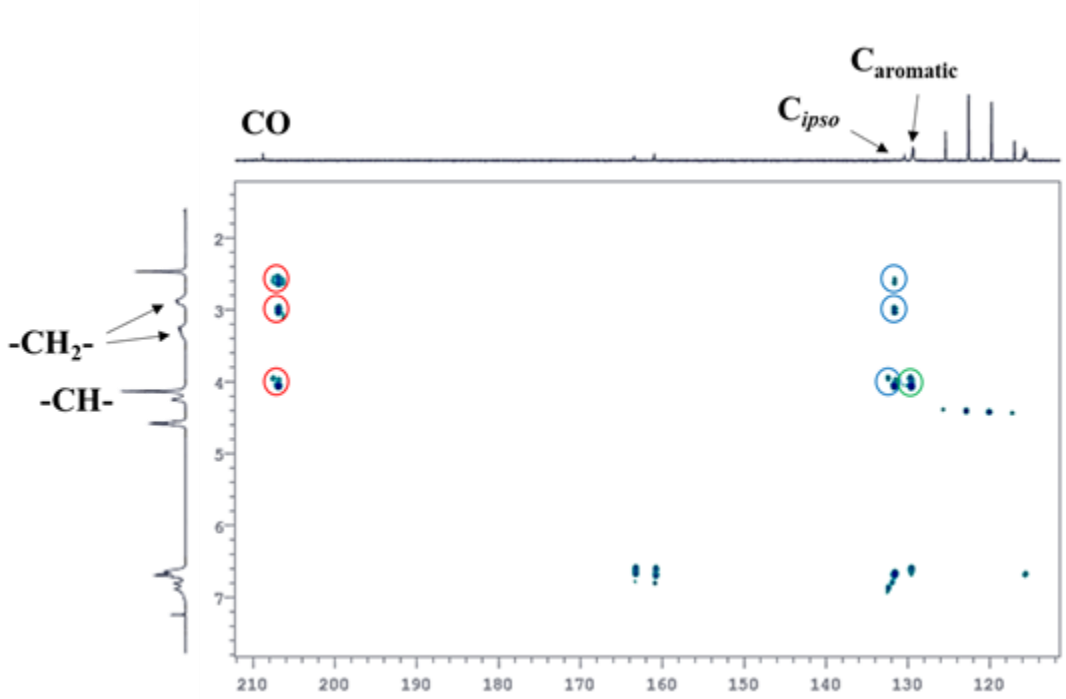

Figure S124. $^{1}H,^{13}C$-HMBC spectrum ($CDCl_3$/HFIP, T = 298 K) of CO/FS copolymer obtained with **4b**.

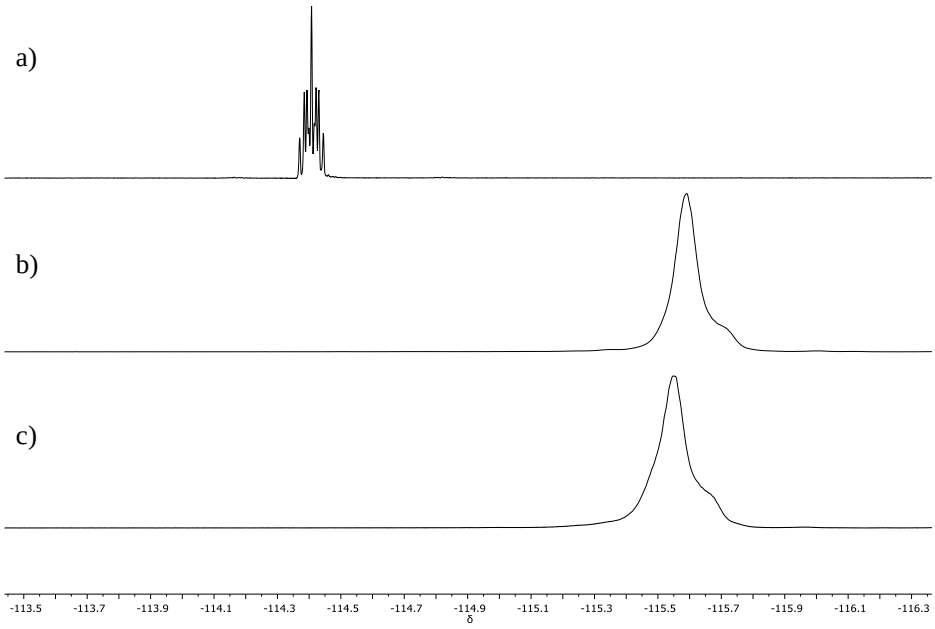

Figure S125. ^{19}F NMR spectrum (T = 298 K) of (a) 4-fluorostyrene (in $CDCl_3$) and of CO/4-fluorostyrene copolymers (in $CDCl_3$/HFIP) obtained with (b) [Pd(CH_3)(CH_3CN)(**phen**)][PF_6] e (c) **4b**.

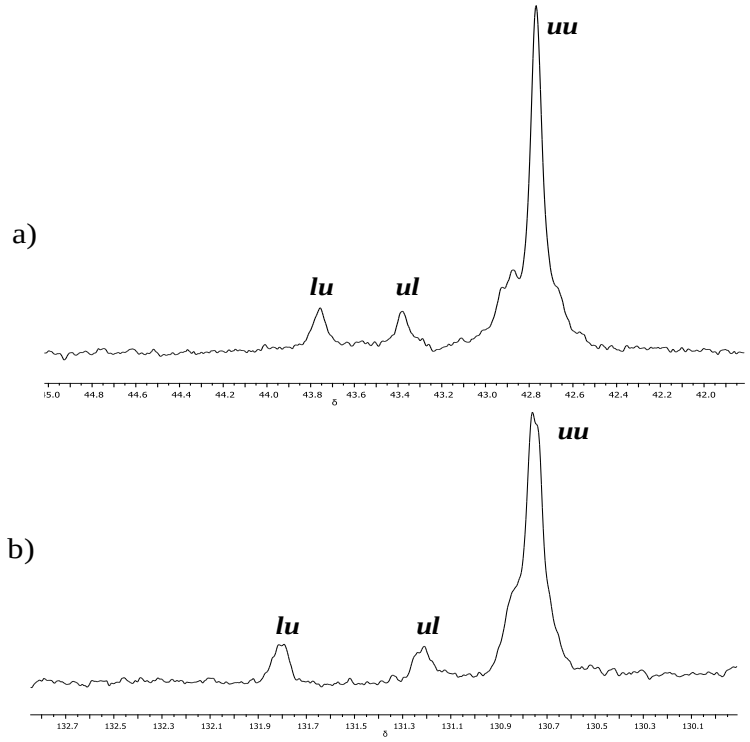

Figure S126. ^{13}C NMR spectrum ($CDCl_3$/HFIP, T = 298 K) of CO/FS copolymer obtained with [Pd(CH_3)(CH_3CN)(**phen**)][PF_6]. (a) CH_2 region; (b) C_{ipso}.

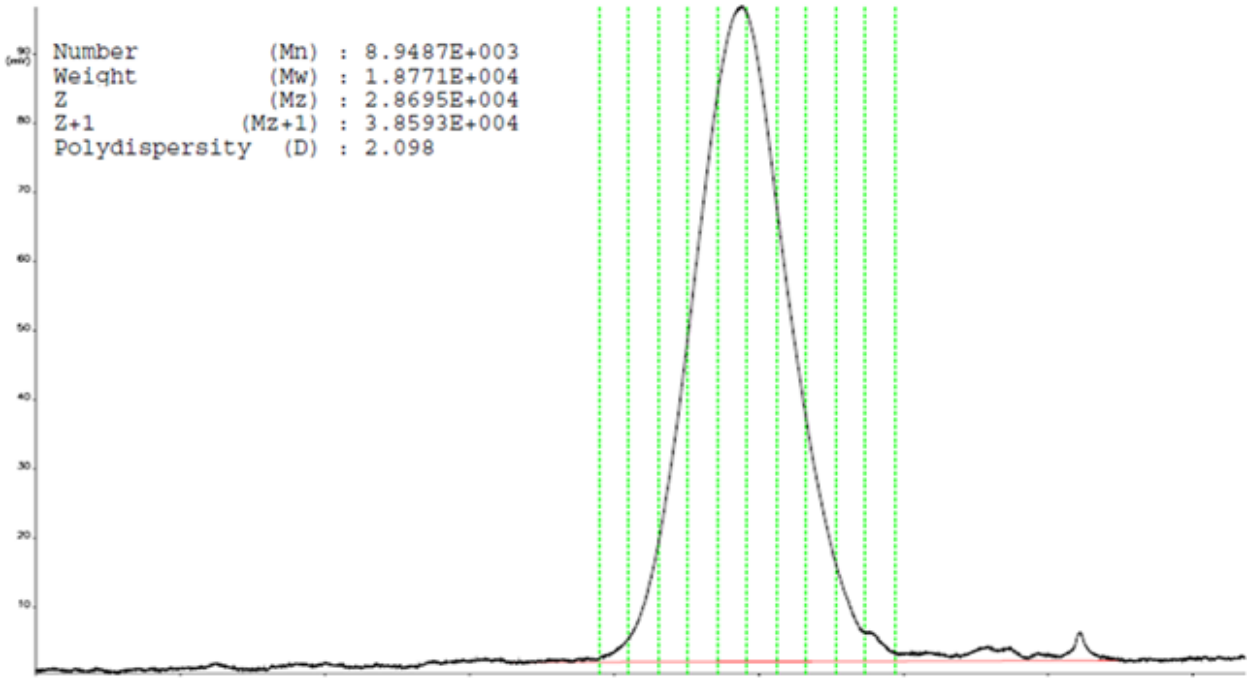

Figure S127. GPC curve for CO/S copolymer obtained with **4b**. Measurement performed on a Knauer HPLC (K-501 Pump, K-2501 UV detector). Statistical calculations: Bruker Chromstar software.

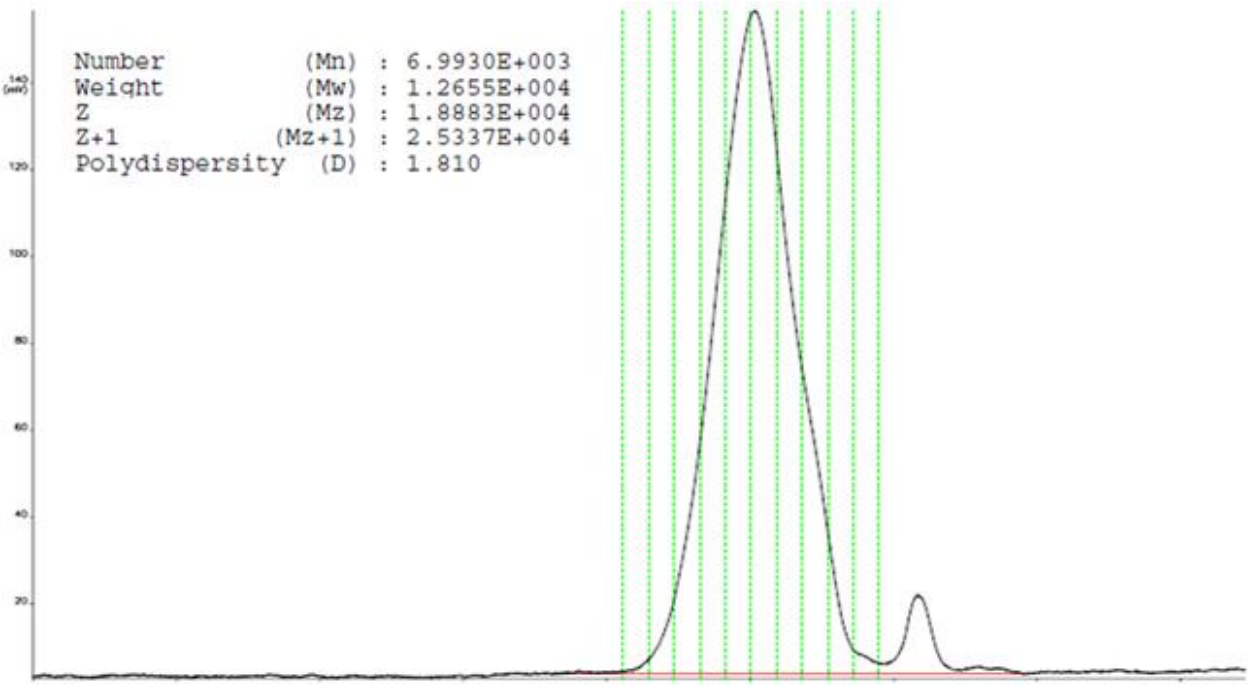

Figure S128. GPC curve for CO/MS copolymer obtained with **4b**. Measurement performed on a Knauer HPLC (K-501 Pump, K-2501 UV detector). Statistical calculations: Bruker Chromstar software.

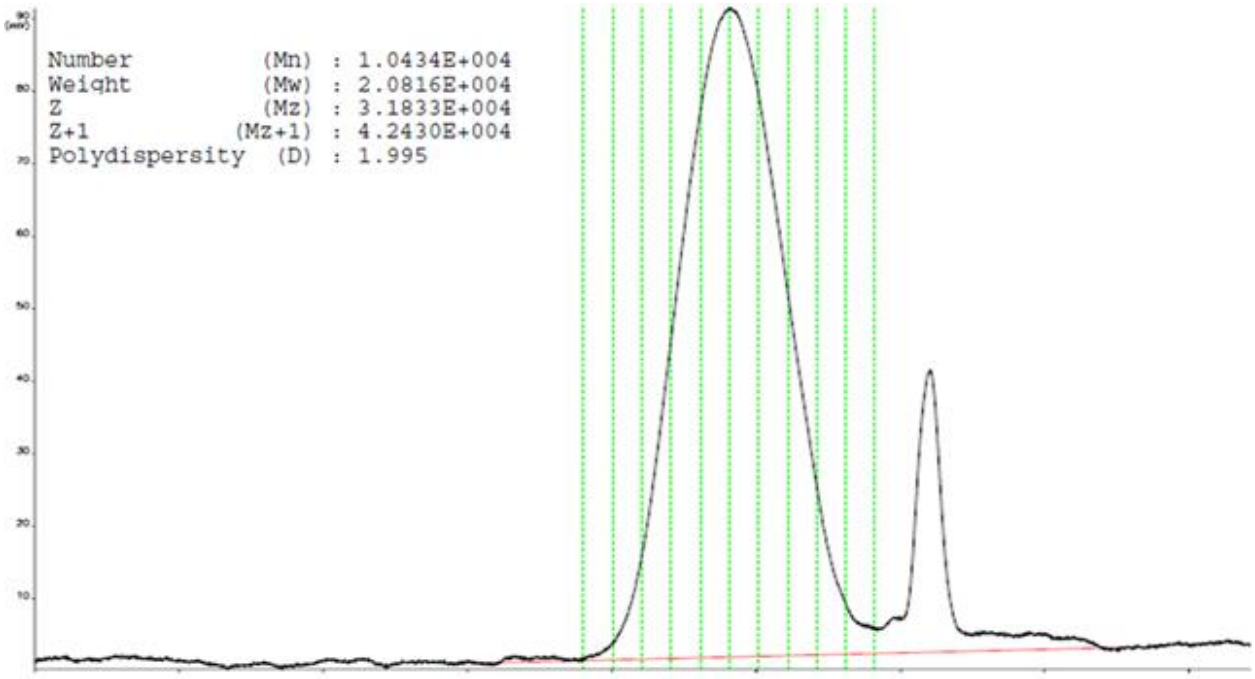

Figure S129. GPC curve for CO/TBS copolymer obtained with **4b**. Measurement performed on a Knauer HPLC (K-501 Pump, K-2501 UV detector). Statistical calculations: Bruker Chromstar software.

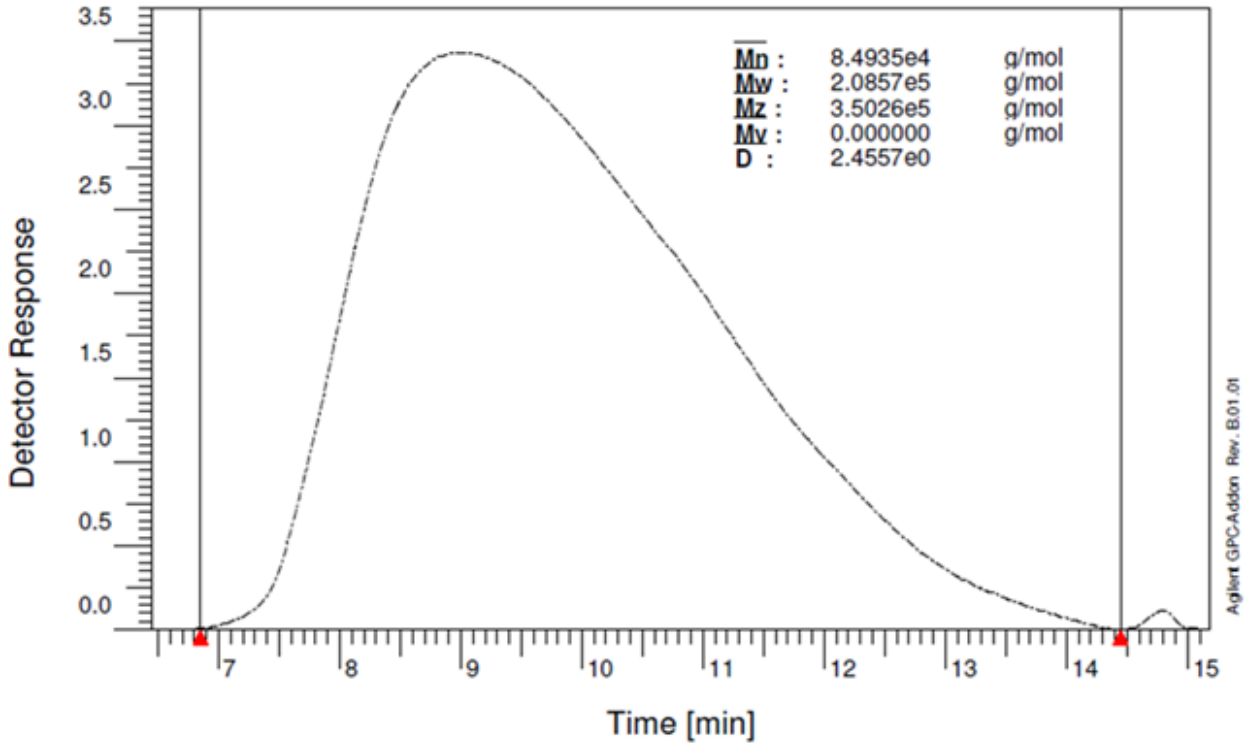

Figure S130. GPC curve for CO/S copolymer obtained with **5b**.

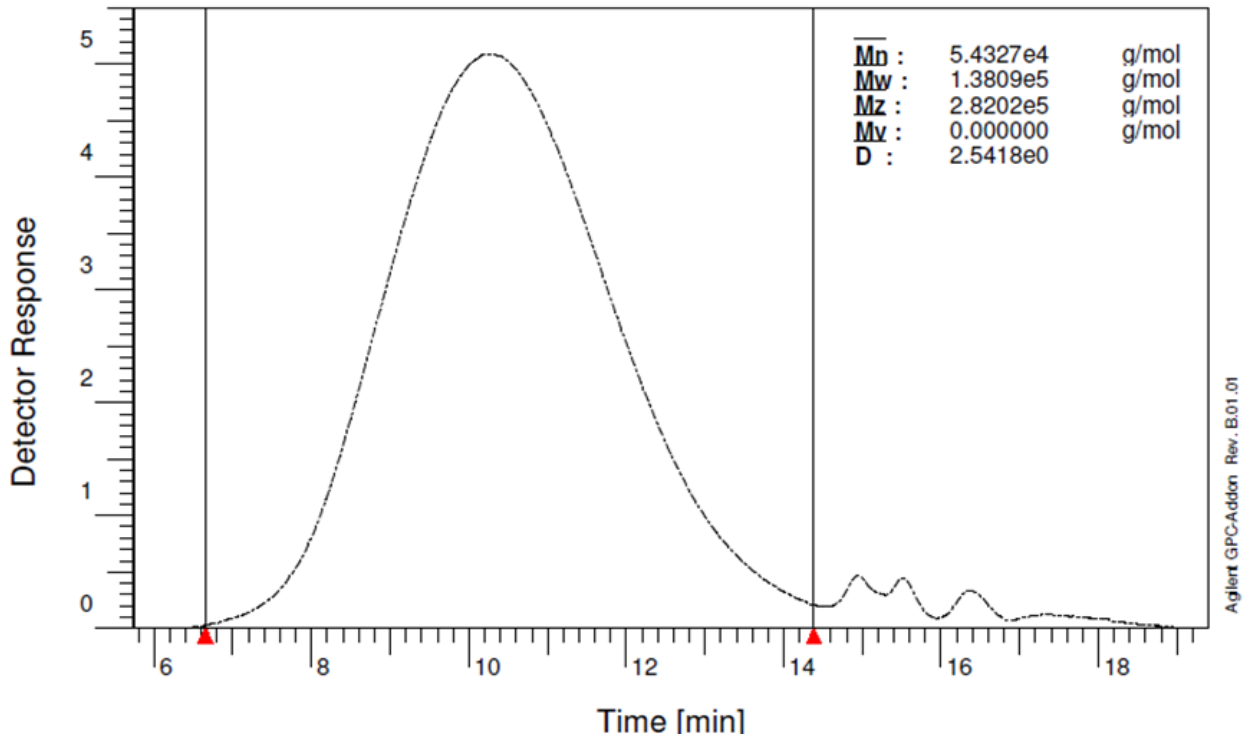

Figure S131. GPC curve for CO/MS copolymer obtained with **5b**.

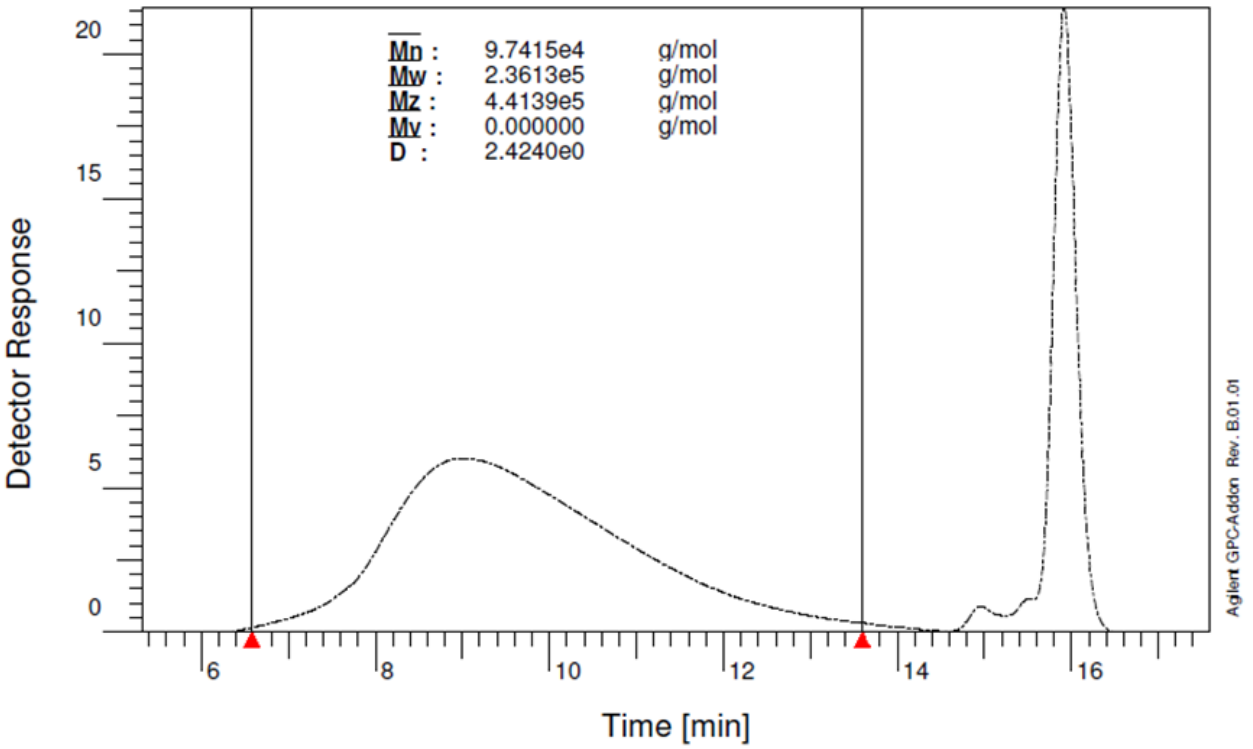

Figure S132. GPC curve for CO/TBS copolymer obtained with **5b**.